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有機リン化合物合成のための資料集

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Tables for Syntheses of Organophosphorus Compounds.

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有機リン化合物のうち比較的用いる機会の多いと思われる化合物について、その合成法および性質、特に前者を簡単かつ正確に知るための表の作成を目的とした。リンを含まない (C, H, O, N, S, ハロゲンよりなる) 有機化合物の合成については少し古いが、R.B. Wagner および H.D. Zook による “*Synthetic Organic Chemistry*” (John Wiley & Sons, Inc., 1953) があるが、ここではその “リン版” となるような表の作成を心がけた。化合物の選択にはかなりの任意性があるが、常識的によく使用する機会のあると思われる置換基の組合せを

一応の目安とした。したがって、その化合物自体は興味あるものであっても、あまり特殊なものは除かれている。

有機リン化合物の合成に関しては K. Sasse による詳細で優れた大著 (*Methoden der Organischen Chemie* (Houben-Weyl), XII/1, XII/2, ed. by E. Müller, Georg Thieme Verlag, Stuttgart, 1963, 1964) があるが、これは 1961 年位までの文献をもとにして書かれたものである。また最近、萩原、熊田、大河原氏らにより *Handbook of Organometallic Compounds* (W.A. Benjamin, Inc., New York, 1968) が刊行され、これにも多数のリン化合物についての性質、合成法などがまとめられているが、この本にあげられている文献は必ずしも合成方法として良いことを基準として選ばれていないと考えられ

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る。

この資料集では、その化合物を実際に合成する際のもも収率よくかつ信頼しうる方法を書いてある。文献は1967年の Chemical Abstracts までについて調べた。なお前にあげた二つの著書も調査の上で大変参考になった。

この資料集で用いた略語は次の通りである。

XおよびY：特にことわりのないかぎりハロゲン；Z：OまたはS；M：金属（ほとんどの場合はアルカリ金属）；g：好収率；q：定量的；dec：分解；subl：昇華

物理定数の項でカッコのない数字は融点を，カッコ内の数字は沸点および減圧度（mmHg）を示している（たとえば（100/5）は b.p. 100°C/5 mmHg を示す）。

I. phosphoranes, phosphonium salts (R_5P , $R_3P=CR_2$, R_4PX)

分子式	構造式	化合物名	方法	収率	文献	物理定数
$C_4H_{12}ClP$	Me_4PCl	Tetramethylphosphonium chloride	1	89	1	396~397
			2	100	2	
$C_4H_{12}IP$	Me_4PI	Tetramethylphosphonium iodide	1	—	3	300
			3	43.5	4	
$C_6H_{20}IP$	Et_4PI	Tetraethylphosphonium iodide	1	77.5	5	280~284
			3	84.8	6	
			3	45	8	
$C_9H_{14}IP$	Me_3PhPI	Trimethylphenylphosphonium iodide	1	107	7	237~238
			3	60	8	
$C_{10}H_{15}ClNP$	$(CH_2)_4(NH_2)PhPCl$	P-Phenyl-P, P-(cycloctetramethylene) phosphonium chloride	6	—	36a	
$C_{10}H_{16}IP$	$Me_2EtPhPI$	Ethyl dimethylphenylphosphonium iodide	1	94	9	150~151
$C_{10}H_{24}IP$	$MePr_3PI$	Methyl tripropylphosphonium iodide	1	—	10	212.5
$C_{11}H_{17}ClNP$	$(CH_2)_5(NH_2)PhPCl$	P-Phenyl-P, P-(cyclopentamethylene) phosphonium chloride	6	—	36a	
$C_{11}H_{18}BrP$	$Me_2PrPhPBr$	Dimethylphenylpropylphosphonium bromide	1	—	11	118
$C_{12}H_{18}IP$	$EtPh(CH_2)_4PI$	Ethylphenyltetramethylenephosphonium iodide	1	—	12	122
$C_{12}H_{20}BrP$	Et_3PhPBr	Triethylphenylphosphonium bromide	3	—	13	184~186
$C_{12}H_{20}IP$	Et_3PhPI	Triethylphenylphosphonium iodide	3	91	8	137~139
			4	84	7	
			1	77	14	
$C_{12}H_{20}IP$	$MeEtPrPhPI$	Ethylmethylphenylpropylphosphonium iodide	1	—	11	62
$C_{12}H_{28}BrP$	Et_2Bu_2PBr	Diethyldibutylphosphonium bromide	5	—	15	146~148
$C_{12}H_{29}ClNP$	Bu_3NH_2PCl	P-tributylaminophosphonium chloride	6	92	16	62~65
$C_{13}H_{20}IP$	$EtPh(CH_2)_5PI$	Ethylpentamethylenephylphosphonium iodide	1	—	17	188
$C_{13}H_{30}IP$	$MeBu_3PI$	Tributylmethylphosphonium iodide	1	—	18	133.5
$C_{13}H_{30}IP$	Pr_3BuPI	Butyl tripropylphosphonium iodide	1	—	3	239~240
$C_{14}H_{16}BrP$	Me_2Ph_2PBr	Dimethyldiphenylphosphonium bromide	1	85	19	216~219
$C_{14}H_{16}IP$	Me_2Ph_2PI	Dimethyldiphenylphosphonium bromide	7	88	20	249.5~251
			8	85	21	
			3	82	21	
$C_{14}H_{24}BrP$	$MeEtBuPhCH_2PBr$	Benzylbutylethylmethylphosphonium bromide	1	—	22	134~136
$C_{14}H_{24}IP$	$MePrBuPhPI$	Butylmethylphenylpropylphosphonium iodide	9	30	23	155~152.5
$C_{14}H_{28}IP$	$Me_2(c-C_6H_{11})_2PI$	Dicyclohexyldimethylphosphonium iodide	3	65	21	217.5
			8	45	24	~218.5
$C_{15}H_{18}BrP$	$MeEtPh_2PBr$	Ethylmethyldiphenylphosphonium bromide	1	—	22	174
$C_{15}H_{18}IP$	$Me_2PhPhCH_2PI$	Benzyl dimethylphenylphosphonium iodide	1	83	7	172~173
$C_{16}H_{18}BrP$	$Me_3C_{13}H_9PBr$	Fluoren-9-yltrimethylphosphonium bromide	1	51	25	221~223
$C_{16}H_{20}BrP$	$MeEtPhPhCH_2PBr$	Benzylethylmethylphenylphosphonium bromide	1	82.5	26	145
$C_{16}H_{20}BrP$	$Me_2(PhCH_2)_2PBr$	Dibenzyl dimethylphosphonium bromide	1	72	27	141~142

分 子 式	構 造 式	化 合 物 名	方法	収 率	文献	物 理 定 数
C ₁₆ H ₂₀ IP	MeEtPhPhCH ₂ PI	Benzylethylmethylphenylphosphonium iodide	1	90	28	167~168
			1	80	9	
C ₁₆ H ₂₀ IP	Et ₂ Ph ₂ PI	Diethyldiphenylphosphonium iodide	7	75	20	209~210
			11	48	29	
C ₁₆ H ₃₆ BrP	Bu ₄ PBr	Tetrabutylphosphonium bromide	1	89.5	5	99~101
C ₁₇ H ₂₀ BrP	Me(CH ₂ =CHCH ₂) PhPhCH ₂ PBr	Allylbenzylmethylphenylphosphonium bromide	1	—	11	142
C ₁₇ H ₂₂ BrP	MePrPhPhCH ₂ PBr	Benzylmethylphenylpropylphosphonium bromide	1	—	11	185
C ₁₇ H ₂₂ IP	MeEt(PhCH ₂) ₂ PI	Dibenzylethylmethylphosphonium iodide	10	84	9	122.5~123
C ₁₈ H ₁₇ BrNP	Ph ₃ NH ₂ PBr	P-(triphenyl)aminophosphonium bromide	12	90	30	248~250
			13	54	31	
C ₁₈ H ₁₇ ClNP	Ph ₃ NH ₂ PCl	P-(triphenyl)aminophosphonium chloride	6	88	32	230~232
C ₁₈ H ₂₂ BrP	Et(CH ₂ =CHCH ₂) PhPhCH ₂ PBr	Allylbenzylethylphenylphosphonium bromide	1	—	22	149~152
C ₁₈ H ₂₄ BrP	Et ₂ (PhCH ₂) ₂ PI	Dibenzyl-diethylphosphonium iodide	5	—	15	234~238
C ₁₈ H ₂₄ IP	EtBuPh ₂ PI	Butylethyl-diphenylphosphonium iodide	1	91	33	153
C ₁₈ H ₁₇ Cl ₂ P	(ClCH ₂)Ph ₃ PCl	Chloromethyltriphenylphosphonium chloride	14	77	23	260~261
C ₁₈ H ₁₈ BrP	MePh ₃ PBr	Methyltriphenylphosphonium bromide	1	89	34	234~235
			15	83	35	
C ₁₈ H ₁₈ ClOP	(HOCH ₂)Ph ₃ PCl	Hydroxymethyltriphenylphosphonium chloride	17	90	23	190~192
C ₁₈ H ₁₈ IP	MePh ₃ PI	Methyltriphenylphosphonium iodide	18	91	20	188~189
C ₁₈ H ₁₈ ClP	Bu ₃ PhCH ₂ PCl	Benzyltributylphosphonium chloride	1	40	37	164.3
C ₂₀ H ₁₇ BrNP	(NCCH ₂)Ph ₃ PBr	Cyanomethyltriphenylphosphonium bromide	1	95	38	~164.5
C ₂₀ H ₁₈ BrP	(CH ₂ =CH)Ph ₃ PBr	Triphenylvinylphosphonium bromide	16	86	36	186~190
C ₂₀ H ₂₀ BrP	EtPh ₃ PBr	Ethyltriphenylphosphonium bromide	1	96	39	205~206
C ₂₀ H ₂₀ ClOP	(HOCH ₂ CH ₂)Ph ₃ PCl	2-hydroxyethyltriphenylphosphonium chloride	1	80	40	233~236
C ₂₀ H ₂₀ IP	EtPh ₃ PI	Ethyltriphenylphosphonium iodide	18	95	20	164~165
			11	70	29	
C ₂₀ H ₂₀ IP	MePh ₂ PhCH ₂ PI	Benzylmethyldiphenylphosphonium iodide	18	89	20	229~230
			19	61	41	
C ₂₀ H ₂₈ IP	Bu ₂ Ph ₂ PI	Dibutyldiphenylphosphonium iodide	1	—	42	154~155
C ₂₁ H ₁₉ INP	(NCCH ₂ CH ₂)Ph ₃ PI	2-Cyanoethyltriphenylphosphonium iodide	20	85	43	187
C ₂₁ H ₂₀ BrP	(CH ₂ =CHCH ₂)Ph ₃ PBr	Allyltriphenylphosphonium bromide	1	100	5	209~214
C ₂₁ H ₂₀ BrOP	(MeCOCH ₂)Ph ₃ PBr	Acetyltriphenylphosphonium bromide	1	44	44	226
C ₂₁ H ₂₀ BrO ₂ P	(MeO ₂ CCH ₂)Ph ₃ PBr	Carbomethoxymethyltriphenylphosphonium bromide	26	97	45	162
			1	90	38	
C ₂₁ H ₂₀ ClO ₂ P	(MeO ₂ CCH ₂)Ph ₃ PCl	Carbomethoxymethyltriphenylphosphonium chloride	1	92	46	149~150
C ₂₁ H ₂₂ BrP	PrPh ₃ PBr	Triphenylpropylphosphonium bromide	1	84.5	47	229~230
C ₂₁ H ₂₂ IP	MePh(PhCH ₂) ₂ PI	Dibenzylmethylphenylphosphonium iodide	10	82	9	207~208
C ₂₂ H ₂₂ BrO ₂ P	(EtO ₂ CCH ₂)Ph ₃ PBr	Carbethoxymethyltriphenylphosphonium bromide	1	—	48	157
C ₂₂ H ₂₂ ClO ₂ P	(EtO ₂ CCH ₂)Ph ₃ PCl	Carbethoxymethyltriphenylphosphonium chloride	1	89	49	144
C ₂₂ H ₂₄ BrP	Me(PhCH ₂) ₃ PBr	Tribenzylmethylphosphonium bromide	1	74	27	229~229.5
C ₂₂ H ₂₄ BrP	BuPh ₃ PBr	Butyltriphenylphosphonium bromide	1	90.8	5	249~251
C ₂₂ H ₂₄ BrP	EtPh(PhCH ₂) ₂ PBr	Dibenzylethylphenylphosphonium bromide	1	—	22	180~183
C ₂₃ H ₂₆ BrP	Et(PhCH ₂) ₃ PBr	Tribenzylethylphosphonium bromide	1	—	22	204
C ₂₄ H ₂₀ BrP	Ph ₄ PBr	Tetraphenylphosphonium bromide	24	91	50	288

分 子 式	構 造 式	化 合 物 名	方法	收 率	文献	物 理 定 数
			23	72.7	51	
			22	98	52	
$C_{24}H_{20}IP$	Ph_4PI	Tetraphenylphosphonium iodide	11	78	29	337
$C_{24}H_{28}BrP$	$BuPh(PhCH_2)_2PBr$	Dibenzylbutylphenylphosphonium bromide	1	—	22	159
$C_{25}H_{22}ClP$	Ph_3PhCH_2PCl	Benzyltriphenylphosphonium chloride	1	100	53	287~288
			25	10	54	
$C_{26}H_{24}BrOP$	$(PhOCH_2CH_2)_3Ph_3PBr$	Phenoxyethyltriphenylphosphonium bromide	1		36	
$C_{26}H_{28}IO_4P$	$EtO_2CCH_2CH(CO_2Et)_2Ph_3PI$	1, 2-Bis(carbethoxy) ethyltriphenylphosphonium iodide	20	69	43	104
$C_{27}H_{24}ClP$	$Ph_3(PhCH=CHCH_2)PCl$	Cinnamyltriphenylphosphonium chloride	1	91~93	55	224~226
$C_{27}H_{24}ClOP$	$Ph_3Ph(COCH_3)CH_2PCl$	Phenylacetyltriphenylphosphonium chloride	26	47	56	172~173
$C_{27}H_{26}IP$	$Ph(PhCH_2)_3PI$	Tribenzylphenylphosphonium iodide	4	—	7	199~201
$C_{28}H_{28}IP$	$(PhCH_2)_4PI$	Tetrabenzylphosphonium iodide	21	—	76	191
			1		78	
$C_{31}H_{24}BrP$	$Ph_3(C_{13}H_9)PBr$	Fluoren-9-yltriphenylphosphonium bromide	1	50	57	307~310
			25	32	54	
$C_{18}H_{16}NP$	$Ph_3P=NH$	P, P, P-(Triphenyl)phosphineimide	27	85	58	128
			28	83	32	
			28	92	77	
$C_{19}H_{15}Cl_2P$	$Ph_3P=CCl_2$	Dichloromethylenetriphenylphosphorane	29		59	
			29		60	
			42		93	
$C_{19}H_{16}ClP$	$Ph_3P=CHCl$	Chloromethylenetriphenylphosphorane	29		61	
			30		62	
$C_{19}H_{17}P$	$Ph_3P=CH_2$	Methylenetriphenylphosphorane	30		63	
$C_{20}H_{16}BrOP$	$Ph_3P=CBrCHO$	Bromotriphenylphosphoranylideneacetaldehyde	31	83	64	180~181
$C_{20}H_{16}NP$	$Ph_3P=CHCN$	Triphenylphosphoranylideneacetonitrile	32	90	65, 66	190~192
$C_{20}H_{17}OP$	$Ph_3P=CHCHO$	Triphenylphosphoranylideneacetaldehyde	33	81	67	186~187
			33	67	68	
$C_{20}H_{18}NOP$	$Ph_3P=CHCONH_2$	Triphenylphosphoranylideneacetamide	30		66	177~178
$C_{20}H_{19}P$	$Ph_3P=CHMe$	Ethylidenetriphenylphosphorane	30		68, 70	
$C_{21}H_{19}O_2PS$	$Ph_3P=CHSO_2Me$	(Methylsulfonyl)methylenetriphenylphosphorane	30	65	71	201~203
$C_{20}H_{20}NP$	$Ph_3P=NEt$	N-Ethyl-P, P, P-triphenylphosphineimide	28	98.3	72	96(198/2)
$C_{20}H_{20}N_2O_2PS$	$Ph_3P=NSO_2NEt_2$	N, N-Diethyl-N'-(triphenylphosphoranylidene)sulfamide	43	66	94	127
$C_{21}H_{15}N_2P$	$Ph_3P=C(CN)_2$	Triphenylphosphoranylidene malononitrile	35	70	73	187~188
			26	42	74	
$C_{21}H_{18}BrO_2P$	$Ph_3P=CBrCO_2Me$	Methylbromo(triphenylphosphoranylidene)acetate	31	96	64	167~168
			31	90	75	
$C_{21}H_{19}P$	$Ph_3P=CHCH=CH_2$	Triphenylvinylmethylenephosphorane	30		63	
$C_{21}H_{19}OP$	$Ph_3P=C(CHO)Me$	1-(Triphenylphosphoranylidene)propionaldehyde	33		68	220~222
			33		56	
$C_{21}H_{19}OP$	$Ph_3P=CHCOMe$	Triphenylphosphoranylidene-2-propanone	30	71	40	205~206
			36	78	79	
$C_{21}H_{19}O_2P$	$Ph_3P=CHCO_2Me$	Methyltriphenylphosphoranylideneacetate	30	65	45	161

分 子 式	構 造 式	化 合 物 名	方法	収 率	文献	物 理 定 数
C ₂₁ H ₂₁ P	Ph ₃ P=CMe ₂	Triphenylisopropylidenephosphorane	30		80,81	
C ₂₁ H ₂₁ P	Ph ₃ P=CH ₂ Et	Triphenyl- <i>n</i> -propylidenephosphorane	30		81	
C ₂₂ H ₁₈ NO ₂ P	Ph ₃ P=C(CN)CO ₂ Me	Methyl triphenylphosphoranylideneacyanoacetate	35	83	73	212~213
C ₂₂ H ₂₁ O ₂ P	Ph ₃ P=CHCO ₂ Et	Ethyl triphenylphosphoranylideneacetate	30	95	82	126~127
C ₂₂ H ₂₃ P	Ph ₃ P=CMeEt	<i>sec</i> -Butylidenetriphenylphosphorane	30		81	
C ₂₂ H ₂₃ P	Ph ₃ P=CHPr	<i>n</i> -Butylidenetriphenylphosphorane	30		81	
C ₂₃ H ₁₉ P	Ph ₃ P=C(CH) ₄	Cyclopentadienylidenetriphenylphosphorane	37	46	83	228~231
C ₂₄ H ₂₀ NP	Ph ₃ P=NPh	N-Phenyl-P, P, P-triphenylphosphine imide	38,39	70	30,84	130~131
C ₂₄ H ₂₃ O ₃ P	Ph ₃ P=C(COMe)(CO ₂ Et)	Ethyl triphenylphosphoranylideneacetoacetate	35	60	73	169~171
C ₂₄ H ₂₃ O ₄ P	Ph ₃ P=C(CO ₂ Me)(CH ₂ CO ₂ Me)	Dimethyl triphenylphosphoranylidenesuccinate	26	80	45	157~158
C ₂₄ H ₂₅ P	Ph ₃ P=C(CH ₂) ₅	Cyclohexylidenetriphenylphosphorane	30		81	
C ₂₄ H ₂₇ P	Ph ₃ P=CH(CH ₂) ₄ CH ₃	<i>n</i> -Hexylidenetriphenylphosphorane	30		69	
C ₂₅ H ₂₀ NO ₂ P	Ph ₃ P=CHC ₆ H ₄ NO ₂ (p)	<i>p</i> -Nitrobenzylidenetriphenylphosphorane	30	33	5	171~172
C ₂₅ H ₂₁ P	Ph ₃ P=CHPh	Benzylidenetriphenylphosphorane	30		56	
C ₂₅ H ₂₅ O ₄ P	Ph ₃ P=C(CO ₂ Et) ₂	Diethyl triphenylphosphoranylidene malonate	35	81	73	106~107
C ₂₅ H ₂₇ OP	Ph ₃ P=C(COEt)Pr	4-Triphenylphosphoranylidene-3-heptanone	26		85	114
C ₂₆ H ₂₁ OP	Ph ₃ P=CHCOPh	2-Triphenylphosphoranylideneacetophenone	30	58	79	178~180
			26	71	40	
			36	80	40	
C ₂₆ H ₂₁ OP	Ph ₃ P=CPhCHO	Phenyltriphenylphosphoranylideneacetaldehyde	30	72	87	124~126
C ₂₆ H ₂₃ P	Ph ₃ P=CMePh	α -Methylbenzylidenetriphenylphosphorane	30		81	
C ₂₆ H ₂₇ O ₃ P	Ph ₃ P=C(CO ₂ Et)COPr	Ethyl 3-oxo-2-triphenylphosphoranylidenehexanoate	26		85	130~131
C ₂₆ H ₂₇ O ₄ P	Ph ₃ P=C(CO ₂ Et)(CH ₂ CO ₂ Et)	Diethyl 2-triphenylphosphoranylidene succinate	30	69	43	104~106
C ₂₇ H ₂₀ NOP	Ph ₃ P=C(COPh)CN	Benzoyltriphenylphosphoranylideneacetonitrile	26		85	208
C ₂₇ H ₂₃ P	Ph ₃ P=CHCH=CHPh	Cinnamylidenetriphenylphosphorane	30		88	
C ₂₇ H ₂₃ OP	Ph ₃ P=CHCOCH ₂ Ph	1-Phenyl-3-triphenylphosphoranylidene-2-propanone	36	42	79	147~148
C ₂₇ H ₂₃ OP	Ph ₃ P=CMeCOPh	2-Triphenylphosphoranylidene propiophenone	36	93	79	170~172
			33	71	89	
C ₂₇ H ₂₃ OP	Ph ₃ P=C(COMe)Ph	1-Phenyl-1-triphenylphosphoranylidene-2-propanone	36	68	79	167~168
			33	73	89	
C ₂₈ H ₂₃ O ₃ P	Ph ₃ P=C(COPh)CO ₂ Me	Methyl benzoyltriphenylphosphoranylideneacetate	33	83	79	133~135
C ₂₈ H ₂₅ OP	Ph ₃ P=CHCOCH ₂ CH ₂ Ph	4-Phenyl-1-triphenylphosphoranylidene-2-butanone	36	80	79	148~150
			33	49	89	
C ₂₈ H ₂₅ O ₂ P	Ph ₃ P=C(CH ₂ Ph)CO ₂ Me	Methyl α -triphenylphosphoranylidenehydrocinnamate	26	75	88,45	185~187
C ₂₉ H ₂₅ OP	Ph ₃ P=C(Me)COCH=CHPh	1-Phenyl-4-triphenylphosphoranylidene-1-penten-3-one	33	73	79	205~208
			36	70	79	
C ₂₉ H ₂₅ O ₃ P	Ph ₃ P=C(COPh)CO ₂ Et	Ethyl benzoyltriphenylphosphoranylideneacetate	35	77	85	142~143
C ₂₉ H ₂₇ OP	Ph ₃ P=C(CMe)COCH ₂ CH ₂ Ph	1-Phenyl-4-triphenylphosphoranylidene-3-pentanone	36	76	79	164~166
			33	50	89	
C ₃₀ H ₂₅ P	Ph ₅ P	Pentaphenylphosphorane	40		91	124(dec)
			41	60	92	
C ₃₁ H ₂₃ P	Ph ₃ P=C(C ₆ H ₄) ₂	Fluoren-9-ylidenetriphenylphosphorane	30	88	25,86	258~260

分子式	构造式	化合物名	方法	收率	文献	物理常数
$C_{31}H_{24}NO_2P$	$Ph_3P=C(Ph)C_6H_4NO_2(p)$	p-Nitro- α -phenylbenzylidenetriphenylphosphorane	30		90	230(dec)
$C_{31}H_{25}P$	$Ph_3P=CPh_2$	Triphenyldiphenylmethylenephosphorane	30		81	
$C_{36}H_{30}N_2O_2P_2S$	$(Ph_3P=N)_2SO_2$	Bis(triphenylphosphoranylidenesulfamide	44	46	94	245.6

方 法

- $R_1R_2R_3P + R_4X \longrightarrow R_1R_2R_3R_4PX$
- $R_4P \cdot \text{picrate} \xrightarrow{HX} R_4PX$
- $R_nPM_{3-n} + R'X \xrightarrow{d} R_nR'_{3-n}PX$
- $(PhP)_4 + RX \xrightarrow{d} R_3PhPX$
- $R_2POPR'(OR') + R'X \longrightarrow R_2R_2''PX$
- $R_3P + NH_2Cl \longrightarrow R_3PNH_2Cl$
- $Ar_nPX_{3-n} + RY \longrightarrow Ar_nR_{4-n}PY$
- $R_2PPR_2 + R'X \longrightarrow R_2R_2'PX$
- $[R_n(CH_2OH)_{4-n}P]X \xrightarrow[2) R'Y]{1) OH^-} R_nR'_{4-n}PY$
- $R_nPX_{3-n} \xrightarrow[2) R''Y]{1) R'MgX} R_nR'_{3-n}R''PY$
- $R_nAr_{3-n}P + Ar'X + R'MgX + CoX_2 \longrightarrow R_mAr'_{n+1-m}Ar_{3-n}PX$
- $Ar_3PX_2 + NH_3 \xrightarrow{Base} Ar_3PNH_2X$
- $Ar_3PX_2 + NH_2MgX \longrightarrow Ar_3PNH_2X$
- $[R_n(CH_2OH)_{4-n}P]X + SOCl_2 \longrightarrow R_n(CH_2Cl)_{4-n}PX$
- $Ph_3P + Ph_3(CH_2Br)PBr \xrightarrow{EtOH} Ph_3PO + Ph_3(CH_3)PBr$
- $(PhOCH_2CH_2)Ph_3PBr \xrightarrow{AcOEt} (CH_2=CH)Ph_3PBr$
- $Ar_3P + CH_2O + HX \longrightarrow Ar_3(CH_2OH)PX$
- $Ar_3PX_2 + RY \longrightarrow Ar_3RPY$
- $Ph_2PX + PhCH(MgCl)COOMgCl + RY \longrightarrow Ph_2(PhCH_2)RPY$
- $Ph_3P + R_1R_2C=CR_3R_4 + HX \longrightarrow Ph_3(CR_1R_2CHR_3R_4)PX$
- $PH_4I + PhCH_2OH \longrightarrow (PhCH_2)_4PI$
- $R_nAr_{3-n}P + MX + Ar'Y \longrightarrow R_{n-m}Ar'_{m+1}Ar_{3-n}PY$
- $Ar_3P + Ar'MgX \xrightarrow{O_2} Ar_3Ar'PX$
- $ArMgX + PY_3 \xrightarrow{O_2} Ar_4PX$
- $R_3P + R'N_2 \xrightarrow{CuX} R_3R'PX$
- $Ph_3P=CR_1R_2 + R_3X \longrightarrow Ph_3(CR_1R_2R_3)PX + Ph_3P=CR_2R_3$
- $Ph_3PNSi(CH_3)_3 \xrightarrow[H_2SO_4]{i-PrOH} Ph_3P=NH$
- $[Ph_3PNHR]X \xrightarrow{Base} Ph_3P=NR$

- $Ph_3P + :CXY \longrightarrow Ph_3P=CXY$
- $[Ph_3PCHR_1R_2]X \xrightarrow{Base} Ph_3P=CR_1R_2$
- $Ph_3P=CHR + X_2 \longrightarrow Ph_3P=CXR$
- $Ph_3P=CHR^1 + R^2CH=CHR^3 \longrightarrow Ph_3P=CHR^2 + R^1CH=CHR^3$
- $Ph_3P=CHR + HCOX \longrightarrow Ph_3P=C(CHO)X$
X=OEt, imidazolyl
- $Ph_4PX + RCH_2Li \longrightarrow Ph_3P=CHR$
- $Ph_3PX_2 + CH_2R^1R^2 \xrightarrow{Base} Ph_3P=CR^1R^2$
- $Ph_3P=CHR + R'COSEt \longrightarrow Ph_3P=CR(COR')$
- $2Ph_3P + \begin{array}{c} Br \\ \diagup \quad \diagdown \\ C=C \\ \diagdown \quad \diagup \\ Br \end{array} \xrightarrow{NaOH} Ph_3P=\begin{array}{c} \diagup \quad \diagdown \\ C=C \\ \diagdown \quad \diagup \end{array}$
- $Ph_3PX_2 + RNH_2 \xrightarrow{Base} Ph_3P=NR$
- $Ph_3P + RN_3 \longrightarrow Ph_3P=NR + N_2$
- $[Ph_3PNMePh]Br + 2PhLi \longrightarrow Ph_5P$
- $Ph_4PI + PhLi \longrightarrow Ph_5P$
- $Ph_3P + HCCl_3 \xrightarrow{t-BuOH} Ph_3P=CCl_2$
- $R_2NSO_2N=PCl_3 + 3ArMgBr \longrightarrow R_2NSO_2N=PAR_3$
- $Cl_3P=NSO_2N=PCl_3 + 6ArMgBr \longrightarrow (ArP=N)_2SO_2$

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II. phosphines (R_3P)

分子式	构造式	化合物名	方法	収率	文献	物理定数
CH_3P	$MePH_2$	Methylphosphine	1	62	1	(-17.1)
			1	87	2	
C_2H_7P	$EtPH_2$	Ethylphosphine	1	65	3	(25/748)
C_3H_9P	$PrPH_2$	<i>n</i> -Propylphosphine	1	69	3	(54/750)
C_3H_9P	<i>i</i> - $PrPH_2$	<i>i</i> -Propylphosphine	2	—	4	(41)
$C_4H_{11}P$	<i>t</i> - $BuPH_2$	<i>t</i> -Butylphosphine	3	50	5	(54) n_D^{20} 1.4252 d_{20} 0.7363
$C_4H_{11}P$	<i>i</i> - $BuPH_2$	2-Methylpropylphosphine	1	71	3	(63/756)
					6	(78~79.6) n_D^{25} 1.4308 d_{20} 0.693
$C_5H_{13}P$	$C_5H_{11}PH_2$	<i>n</i> -Pentylphosphine	3	48	5	(104) n_D^{20} 1.4431 d_{20} 0.7796
			4	40	7	(104) n_D^{20} 1.4129
C_6H_7P	$PhPH_2$	Phenylphosphine	5	71.5	8	(160)
			6	75	7	(160) n_D^{20} 1.5796 d_{15} 1.001
$C_6H_{13}P$	<i>c</i> - $C_6H_{11}PH_2$	Cyclohexylphosphine	7	90	7	(146) n_D^{20} 1.4895
			5	65	8	(146)
C_7H_9P	$PhCH_2PH_2$	Benzylphosphine	1	75	3	(180)
			4	48	9	(180)
C_2H_7P	Me_2PH	Dimethylphosphine	1	67.2	2	(24)
			8	88	10	(24)
C_3H_9P	$MeEtPH$	Ethylmethylphosphine	9	44	11	(54~55) -160
C_4H_9P	$(CH_2)_4PH$	Phospholane	10	30	12	(105.4) -88
			11	45.3	13	(0/9)
$C_4H_{11}P$	$MePrPH$	Methylpropylphosphine	9	62.8	11	(84~85) -129.5
$C_4H_{11}P$	Et_2PH	Diethylphosphine	8	92	10	(85~85.5)
			9	70	14	
$C_5H_{13}P$	$MeBuPH$	<i>n</i> -Butylmethylphosphine	9	79.8	11	(109~110/715) -107
$C_6H_{15}P$	<i>n</i> - Pr_2PH	Di- <i>n</i> -propylphosphine	34	—	54	131~133
$C_6H_{15}P$	<i>i</i> - Pr_2PH	Di- <i>i</i> -propylphosphine	2	—	4	(118)
C_7H_9P	$PhMePH$	Methylphenylphosphine	12	65	15	(59~60/10) n_D^{20} 1.5695
			9	62.5	11	(55~56/10)

分子式	構造式	化合物名	方法	収率	文献	物理定数
C ₇ H ₁₅ P	<i>c</i> -C ₆ H ₁₁ MePH	Cyclohexylmethylphosphine	12	48	16	(30~31/3)
C ₈ H ₁₁ P	PhEtPH	Ethylphenylphosphine	13	64.3	17	(122~125)
C ₈ H ₁₉ P	Bu ₂ PH	Di- <i>n</i> -butylphosphine	12	62~82	15	(61/10) n_D^{20} 1.4568
C ₈ H ₁₉ P	<i>i</i> -Bu ₂ PH	Diisobutylphosphine	14	52	6	(169.6) -70 n_D^{20} 1.4487
C ₉ H ₂₁ P	PrC ₆ H ₁₃ PH	<i>n</i> -Propyl- <i>n</i> -hexylphosphine	12	61	15	(193.5~195) n_D^{20} 1.4579
C ₁₀ H ₁₅ P	BuPhPH	<i>n</i> -Butylphenylphosphine	12	86	15	(102/9) n_D^{20} 1.5400
C ₁₂ H ₁₁ P	Ph ₂ PH	Diphenylphosphine	15	80	18	(103/1)
C ₁₂ H ₂₃ P	(<i>c</i> -C ₆ H ₁₁) ₂ PH	Dicyclohexylphosphine	9	68.5	14	(281~283)
			16	60.2	14	
C ₁₄ H ₁₅ P	(PhCH ₂) ₂ PH	Dibenzylphosphine	9	45.8	14	(115~120)
C ₃ N ₃ P	(CN) ₃ P	Phosphorus (III) cyanide	32	81	51	200
C ₃ H ₉ P	Me ₃ P	Trimethylphosphine	17	92	2	-88
			18	66*	19	(*CS ₂ adduct)
			20	43	50	
C ₃ H ₉ O ₃ P	(HOCH ₂) ₃ P	Tris(hydroxymethyl)phosphine	19	94	20	(111~113/2.5) 51~3
C ₆ H ₉ P	(CH ₂ =CH) ₃ P	Trivinylphosphine	20	55	21	(58.1/100)
C ₆ H ₁₁ P	HC≡CPEt ₂	Diethylethynylphosphine	21	49	22	(66~67/77) n_D^{20} 1.4808
C ₆ H ₁₃ P	(CH ₂) ₄ PEt	Ethylcyclotetramethylenephosphine	11	22	23	(145~147)
C ₆ H ₁₅ P	Me ₂ BuP	<i>n</i> -Butyldimethylphosphine	22	44.4	24	69~70/100 d_{20} 0.8455 n_D^{20} 1.4458
C ₆ H ₁₅ P	Et ₃ P	Triethylphosphine	18	62	19	(CS ₂ adduct)
			20	60~80	19a	(127)
C ₇ H ₁₅ P	(CH ₂) ₅ PEt	Ethylcyclopentamethylenephosphine	11	19.7	23	(170)
C ₈ H ₁₁ P	Me ₂ PhP	Dimethylphenylphosphine	27	69	33	(85~86/13)
C ₈ H ₁₁ O ₂ P	Ph(CH ₂ OH) ₂ P	Phenylbis(hydroxymethyl) phosphine	23	—	25	oil
C ₈ H ₁₅ P	Pr ₂ (C≡CH)P	Ethynyldipropylphosphine	21	60	22	(55/11) n_D^{20} 1.4770
C ₈ H ₁₇ P	Pr ₂ (CH=CH ₂)P	Di- <i>n</i> -propylvinylphosphine	24	68	26	(68~69/23) n_D^{20} 1.4680 d_{20} 0.8144
C ₈ H ₁₉ P	MeEtC ₆ H ₁₁ P	Methylethyl- <i>n</i> -pentylphosphine	25	71	27	(74~74.5/22) n_D^{20} 1.4574
C ₈ H ₁₉ P	Et ₂ BuP	Diethylbutylphosphine	22	72	24	(110~111/100) n_D^{20} 1.4596 d_{20} 0.8094
C ₉ H ₁₁ P	Me(CH ₂ =CH)PhP	Methylvinylphenylphosphine	24	59	26	(90~90.5/13) n_D^{20} 1.5732 d_{20} 0.9741
C ₁₂ H ₂₇ P	Bu ₃ P	Tri- <i>n</i> -butylphosphine	20	57	52	(149~150/50)
C ₁₃ H ₁₃ P	Ph ₂ MeP	Methyldiphenylphosphine	26	60	8	(284)
C ₁₃ H ₂₁ P	PhEtC ₆ H ₁₁ P	Ethyl- <i>n</i> -pentylphenylphosphine	21	59.9	28	(129~131/10) n_D^{20} 1.5299 d_{20} 0.9237
C ₁₄ H ₁₃ P	C ₆ H ₄ (CH ₂) ₂ PPh	2-Phenylisophosphaindoline	29		29	(182~186/15)
C ₁₄ H ₁₃ P	(CH ₂ =CH)Ph ₂ P	Diphenylvinylphosphine	21	31.5	30	(117.5~119/0.6)
			21	56.8	31	(104/0.25) $n_D^{24.5}$ 1.6260
C ₁₄ H ₁₃ OP	(MeCO)Ph ₂ P	Acetyldiphenylphosphine	17	39.8	32	(143~146/2.5)
C ₁₄ H ₁₅ P	MePhPhCH ₂ P	Methylbenzylphenylphosphine	27	85	33	(156~158/12)
C ₁₄ H ₁₅ P	EtPh ₂ P	Ethylidiphenylphosphine	26	52	8	(293)
			27	59	33	
C ₁₄ H ₂₅ P	EtC ₆ H ₁₃ PhP	Ethyl- <i>n</i> -hexylphenylphosphine	21	—	34	(123~125), (120~124)
			29	40	35	n_D^{20} 1.5255 d_{20} 0.9212
C ₁₄ H ₂₃ P	PrBuPhCH ₂ P	Benzyl- <i>n</i> -butyl- <i>n</i> -propylphosphine	30	—	36	(113~115) n_D^{20} 1.5090 d_{20} 0.9467
C ₁₄ H ₂₇ P	(<i>c</i> -C ₆ H ₁₁) ₂ EtP	Ethylidicyclohexylphosphine	21	42	37	(155~157/10)
C ₁₅ H ₁₅ P	(CH ₂ =CHCH ₂)Ph ₂ P	Allyldiphenylphosphine	26	52	8	(194~200/15)

分子式	构造式	化 合 物 名	方法	收 率	文献	物 理 定 数
$C_{15}H_{17}P$	$i\text{-PrPh}_2P$	Isopropylidiphenylphosphine	17	65.5	38	(165/13)
			27	25	33	
$C_{15}H_{17}P$	EtPhPhCH_2P	Ethylbenzylphenylphosphine	27	91	33,39	(168/12)
			29	—	36	(165~8/13) n_D^{20} 1.5960 d_{20} 1.0393
$C_{16}H_{19}P$	$(\text{PhCH}_2)_2\text{EtP}$	Dibenzylethylphosphine	27	90	33	(143~145/1)
$C_{16}H_{19}P$	BuPh_2P	n -Butyldiphenylphosphine	17	61	38	(180~182/0.4) n_D^{20} 1.5931
			25	54	40	(140/0.45)
$C_{16}H_{19}P$	$\text{PrPhCH}_2\text{PhP}$	n -propylbenzylphenylphosphine	27	82	33,39	(173~174/12)
			29	—	36	(172~5/12) n_D^{20} 1.5680
$C_{17}H_{21}P$	BuPhPhCH_2P	n -Butylbenzylphenylphosphine	27	81	33	(151~152/3)
			29	—	36	(184~190/11) n_D^{20} 1.5729 d_{20} 1.0112
$C_{18}H_{15}P$	Ph_3P	Triphenylphosphine	20	90	41	79.5
$C_{19}H_{15}OP$	$(\text{PhCO})\text{Ph}_2P$	Benzoyldiphenylphosphine	17	58.6	32	68~81 (199~201/25)
$C_{18}H_{21}P$	$(c\text{-C}_6\text{H}_{11})\text{Ph}_2P$	Cyclohexyldiphenylphosphine	22	60	17	60~61
$C_{18}H_{23}P$	$(\text{PhCH}_2)_2\text{BuP}$	Dibenzyl- n -butylphosphine	29	—	24	(163~178/5) n_D^{20} 1.5678
$C_{18}H_{27}P$	$(c\text{-C}_6\text{H}_{11})_2\text{PhP}$	Dicyclohexylphenylphosphine	30	90	19	56~57
			22	50	17	57~58
$C_{18}H_{33}P$	$(c\text{-C}_6\text{H}_{11})_3P$	Tricyclohexylphosphine	20	47	42	76~78
$C_{19}H_{17}P$	$(\text{PhCH}_2)\text{Ph}_2P$	Diphenylbenzylphosphine	26	53	8	(205~208/1.5)
			21	54	43	142~143(dec) (146~148/0.15)
$C_{20}H_{15}P$	$(\text{PhC}\equiv\text{C})\text{Ph}_2P$	Phenylethynylidiphenylphosphine	21	79	44	43
			17	50	45	
$C_{20}H_{19}P$	$(\text{PhCH}_2)_2\text{PhP}$	Dibenzylphenylphosphine	22	89	43	71~72
				83	53	71~72(176~177/0.3)
$C_{20}H_{27}P$	$(\text{PhC}\equiv\text{C})(c\text{-C}_6\text{H}_{11})_2P$	Dicyclohexylphenylphosphine	17	35	45	74
$C_{21}H_{15}O_3P$	$(\text{PhCO})_3P$	Tribenzoylphosphine	31	—	46	147
$C_{21}H_{18}N_3O_3P$	$(\text{PhNHCO})_3P$	Tris(phenylcarbamoyl)phosphine	34	29	47	212~213
$C_{21}H_{21}P$	$(\text{PhCH}_2)_3P$	Tribenzylphosphine	20	85	48	92~95
$C_{22}H_{17}P$	$(1\text{-C}_{10}\text{H}_7)\text{Ph}_2P$	1-Naphthyldiphenylphosphine	17	86	49	124
			21	33	17	122~124
$C_{24}H_{15}P$	$(\text{PhC}\equiv\text{C})_3P$	Tris(phenylethynyl)phosphine	20	90	44	92

方 法

- $\text{MPH}_2 + \text{RX} \longrightarrow \text{RPH}_2$
- $\text{RI} + \text{PH}_4\text{I} + \text{ZnO} \longrightarrow \text{RPH}_2$
- $\text{PH}_3 \cdot \text{AlCl}_3 + \text{RX} \longrightarrow \text{RPH}_2$
- $\text{RP}(\text{O})(\text{OR}')_2 + \text{LiAlH}_4 \longrightarrow \text{RPH}_2$
- $\text{RPCl}_2 + \text{Na} \xrightarrow{\text{H}_2\text{O}} \text{RPH}_2$
- $\text{RPCl}_2 + \text{LiAlH}_4 \longrightarrow \text{RPH}_2$
- $\text{RP}(\text{O})\text{Cl}_2 + \text{LiAlH}_4 \longrightarrow \text{RPH}_2$
- $\text{R}_2\text{PPR}_2 + \text{Na} \xrightarrow{\text{MeOH}} \text{R}_2\text{PH}$
- $\text{R}_2\text{P}(\text{S})\text{P}(\text{S})\text{R}_2 + \text{LiAlH}_4 \longrightarrow \text{R}_2\text{PH}$
- $\text{R}_2'\text{NP}(\text{CH}_2)_n\text{BH}_3 \xrightarrow{d} (\text{CH}_2)_n\text{PH}$
- $\text{PH}_3 + \text{Na} + \text{X}(\text{CH}_2)_n\text{X} \xrightarrow{\text{liq NH}_3} (\text{CH}_2)_n\text{PH}$
- $\text{RPHM} + \text{R}'\text{X} \longrightarrow \text{RR}'\text{PH}$
- $\text{R}_2\text{PM} \cdot \text{dioxan} + \text{H}_2\text{O} \longrightarrow \text{R}_2\text{PH}$
- $\text{R}_2\text{C}=\text{CR}_2 + \text{PH}_3 \xrightarrow[\text{initiators}]{\text{radical}} \text{R}_2'\text{PH}$
- $\text{Ph}_3\text{P} + \text{Na} \longrightarrow \text{Ph}_2\text{PNa} \xrightarrow{\text{H}_2\text{O}} \text{Ph}_2\text{PH}$
- $\text{R}_2\text{P}(\text{O})\text{Cl} + \text{LiAlH}_4 \longrightarrow \text{R}_2\text{PH}$
- $\text{R}_2\text{PM} + \text{R}'\text{X} \longrightarrow \text{R}_2\text{R}'\text{P}$
- $3\text{RLi} + \text{PCl}_3 \longrightarrow \text{R}_3\text{P}$
- $\text{PH}_3 + \text{RCHO} \longrightarrow (\text{RCHOH})_3\text{P}$
- $\text{PX}_3 + 3\text{RMgX} \longrightarrow \text{R}_3\text{P}$
- $\text{R}_2\text{PX} + \text{R}'\text{MgX} \longrightarrow \text{R}_2\text{R}'\text{P}$
- $\text{RPX}_2 + \text{R}'\text{MgX} \longrightarrow \text{RR}_2'\text{P}$
- $\text{RPH}_2 + \text{R}'\text{CHO} \longrightarrow \text{RP}(\text{R}'\text{CHOH})_2$

24. $R_2POR' + R''MgX \longrightarrow R_2R''P$
25. $R_1R_2R_3R_4PI + LiAlH_4 \longrightarrow R_1R_2R_3P$
26. $R_1R_2R_3R_4PI + 2Na \longrightarrow R_1R_2R_3P$
27. $R_1R_2R_3R_4PI \xrightarrow{\text{electrolysis}} R_1R_2R_3P$
28. $R_1PCl_2 + R_2MgX + R_3MgX \longrightarrow R_1R_2R_3P$
29. $R_1R_2R_3R_4PI \xrightarrow{d} R_1R_2R_3P$
30. $RPCl_2 + R'Li \longrightarrow RR_2'P$
31. $PH_3 + RCOX \xrightarrow{\text{alkali}} P(COR)_3$
32. $PCl_3 + AgCN \longrightarrow P(CN)_3$
33. $R_2PPR_2 + H_2/Cu \longrightarrow 2R_2PH$
34. $[CCl_3CH(OH)]_3PH$

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IIIa dihalogenophosphoranes (R_3PX_2)

分子式	構造式	化合物名	方法	収率	文献	物理定数
$C_3H_9Cl_2P$	Me_3PCl_2	Dichlorotrimethylphosphorane	1	95	1	267~268
$C_3H_9Br_2P$	Me_3PBr_2	Dibromotrimethylphosphorane	1	93	1	277~278
$C_3H_9I_2P$	Me_3PI_2	Diiodotrimethylphosphorane	2	89	1	279~280(dec)
$C_6H_{15}Cl_2P$	Et_3PCl_2	Dichlorotriethylphosphorane	1	—	2	245~250(dec)
$C_6H_{15}Br_2P$	Et_3PBr_2	Dibromotriethylphosphorane	2	86.5	3	253(dec)
$C_6H_{15}I_2P$	Et_3PI_2	Diiodotriethylphosphorane	2	79.8	3	140(dec)
$C_9H_{21}Br_2P$	Pr_3PBr_2	Dibromotri- <i>n</i> -propylphosphorane	2	86.6	3	166(dec)
$C_{12}H_{27}Cl_2P$	Bu_3PCl_2	Dichlorotri- <i>n</i> -butylphosphorane	4	68	4	134~137
$C_{12}H_{27}F_2P$	Bu_3PF_2	Difluorotri- <i>n</i> -butylphosphorane	4	66	5	(71~72/0.4) $n_D^{24} = 1.4320$ $d_4^{25} = 0.9398$
$C_{12}H_{27}I_2P$	Bu_3PI_2	Diiodotri- <i>n</i> -butylphosphorane	2	66.7	3	178(dec)
$C_{18}H_{15}F_2P$	Ph_3PF_2	Difluorotriphenylphosphorane	3	69	6	136~140
			1	67	6	
$C_{18}H_{15}Br_2P$	Ph_3PBr_2	Dibromotriphenylphosphorane	2	—	7	—
$C_{18}H_{15}I_2P$	Ph_3PI_2	Diiodotriphenylphosphorane	2	100	3	148(dec)
$C_{18}H_{15}Cl_2P$	Ph_3PCl_2	Dichlorotriphenylphosphorane	1	96	8	176

IIIb phosphine sulfides ($R_3P=S$)

C_3H_9PS	Me_3PS	Trimethylphosphine sulfide	1	90	2	155~156
			2	49	1	
$C_6H_{15}PS$	Et_3PS	Triethylphosphine sulfide	3	80	3	94.5~95.5
$C_8H_{11}PS$	Me_2PhPS	Dimethylphenylphosphine sulfide	1	88	2	47~47.7
$C_9H_{13}PS$	$MeEtPhPS$	Methylethylphenylphosphine sulfide	1	84	2	33~34 (103~105/0.04)
$C_9H_{21}PS$	Pr_3PS	Tri- <i>n</i> -propylphosphine sulfide	3	61	4	(112/1.1) $n_D^{27} = 1.5071$
$C_{10}H_{15}PS$	$PhEt_2PS$	Diethylphenylphosphine sulfide	3	73	4	(127.5/0.8) $n_D^{25} = 1.5891$
$C_{12}H_{27}PS$	Bu_3PS	Tri- <i>n</i> -butylphosphine sulfide	6	25~40	5	(137~138/1.1) $n_D^{25} = 1.4925$, $d_4^{24} = 1.0339$
$C_{14}H_{13}PS$	$(CH_2=CH)Ph_2PS$	Vinyldiphenylphosphine sulfide	3	67	6	57
$C_{18}H_{15}PS$	Ph_3PS	Triphenylphosphine sulfide	4	82	7	161
			4	80	1	
$C_{19}H_{17}PS$	Ph_2PhCH_2PS	Diphenylbenzylphosphine sulfide	5	59	8	162~163

IIIc phosphine oxides ($R_3P=O$)

$C_3H_5Cl_3OP$	$(ClCH_2)_3PO$	Tris(chloromethyl)phosphine oxide	13	36	1	99.5~100.5
C_3H_9OP	Me_3PO	Trimethylphosphine oxide	1	75	2, 3	140~141
$C_3H_9O_3P$	$(HOCH_2)_3PO$	Tris(hydroxymethyl)phosphine oxide	10	98	33	56~58
$C_4H_{11}OP$	Me_2EtPO	Dimethylethylphosphine oxide	10	47	4	76~77(223~225)
$C_6H_{13}OP$	$(CH_2=CH)Et_2PO$	Diethylvinylphosphine oxide	12	50	5	35~36(62~63/2)
$C_6H_{14}ClOP$	$(ClCH_2CH_2)Et_2PO$	Diethyl- β -chloroethylphosphine oxide	11	70	5	33~34(100~101/0.1)
$C_6H_{15}OP$	Et_3PO	Triethylphosphine oxide	10	57	6	52.9
			1	57	4	(115~117/13)

分子式	構造式	化 合 物 名	方法	収 率	文献	物 理 定 数
C ₇ H ₁₂ OP		3-Methyl-1-ethyl-3-phospholene-1-oxide	6	51	7	(115~119/1.2~1.3) $n_D^{25} = 1.5050$
C ₇ H ₁₇ OP	MePr ₂ PO	Methyldi- <i>n</i> -propylphosphine oxide	7	90	8	39~39.5(91~93/1.0)
C ₈ H ₁₁ OP	Me ₂ PhPO	Dimethylphenylphosphine oxide	8	60	9	107~109(300~308)
C ₈ H ₁₇ OP	(CH ₂ =CH)Pr ₂ PO	Vinyldi- <i>n</i> -propylphosphine oxide	10	97	10	36~37(77~78/1.0, 89~89.5/2)
			12	46	5	
C ₈ H ₁₉ OP	MeEtC ₆ H ₁₁ PO	Methylethyl- <i>n</i> -amylphosphine oxide	10	86	11	8~9(76~76.5/0.4)
C ₉ H ₁₃ OP	MeEtPhPO	Methylethylphenylphosphine oxide	8	89	12	52
			10	86	4	
C ₉ H ₁₅ OP	(CH ₂ =CHCH ₂) ₃ PO	Triallylphosphine oxide	1	26	13	15~17(98/0.5)
C ₁₀ H ₁₁ OP	(CH ₂ =CH) ₂ PhPO	Divinylphenylphosphine oxide	10	92	10	50~51(130~130.5/2)
C ₁₀ H ₁₃ OP	(CH ₂ =CH)EtPhPO	Ethylvinylphenylphosphine oxide	12	58	5	43~44(112~113/1)
C ₁₀ H ₂₁ OP	(CH ₂ =CH)Bu ₂ PO	Vinyldi- <i>n</i> -butylphosphine oxide	10	62	10	37.5~38(103.5~104/1.5)
C ₁₁ H ₁₃ OP		3-Methyl-1-phenyl-3-phospholene-1-oxide	6	57~63	29	60~65(173~174/0.7)
C ₁₂ H ₁₅ OP	(CH ₂ =CHCH ₂) ₂ PhPO	Diallylphenylphosphine oxide	2	56	14	48~50(169/1.3)
C ₁₂ H ₁₉ OP	Pr ₂ PhPO	Dipropylphenylphosphine oxide	2	47.6	14	(121~124/0.5~1.0)
C ₁₂ H ₂₇ OP	Bu ₃ PO	Tri- <i>n</i> -butylphosphine oxide	1	84.4	34	67~69(145~149/3)
C ₁₃ H ₁₃ OP	MePh ₂ PO	Methyldiphenylphosphine oxide	4	65	16	112.5~113
			4	83.5	17	
			6	73	15	
C ₁₄ H ₁₃ OP	(CH ₂ =CH)Ph ₂ PO	Vinyldiphenylphosphine oxide	12	62	18	116.5~118
			10	48	19	
C ₁₄ H ₁₅ OP	EtPh ₂ PO	Ethyldiphenylphosphine oxide	5	62	16	122~123
			3	67.2	20	
C ₁₅ H ₁₇ OP	EtPhPhCH ₂ PO	Ethylphenylbenzylphosphine oxide	8	73	9	112~113
			5	39	16	
C ₁₆ H ₁₉ OP	BuPh ₂ PO	<i>n</i> -butyldiphenylphosphine oxide	10	100	21	95
C ₁₈ H ₁₅ OP	Ph ₃ PO	Triphenylphosphine oxide	10	75~100	22,23,31	156
C ₁₉ H ₁₇ OP	Ph ₂ PhCH ₂ PO	Diphenylbenzylphosphine oxide	3	86	32	195~196
			9	86	25	
			13	64	24	
C ₁₉ H ₁₇ OP	<i>p</i> -CH ₃ C ₆ H ₄ Ph ₂ PO	Diphenyl- <i>p</i> -tolylphosphine oxide	8	90	26	129~130
C ₁₉ H ₁₇ O ₂ P	<i>p</i> -CH ₃ OC ₆ H ₄ Ph ₂ PO	Diphenyl- <i>p</i> -methoxyphenylphosphine oxide	10	93	27	117~118
			8	87	26	
C ₂₀ H ₁₉ OP	Ph(PhCH ₂) ₂ PO	Phenyldibenzylphosphine oxide	10	—	9	180~181
			8	100	28	
C ₁₈ H ₃₃ OP	(<i>c</i> -C ₆ H ₁₁) ₃ PO	Tricyclohexylphosphine oxide	10	65	31	155

方 法 IIIa

1. $3\text{RMgX} + \text{POX}_3 \longrightarrow \text{R}_3\text{P}=\text{O} + 3\text{MgX}_2$
2. $\text{RP}(\text{O})(\text{OR}')_2 + 2\text{R}''\text{OMgX} \longrightarrow \text{RP}(\text{O})\text{R}_2'' + 2\text{R}'\text{OMgX}$
3. $\text{R}_2\text{P}(\text{O})\text{X} + \text{R}'\text{MgX} \longrightarrow \text{R}_3\text{P}(\text{O})\text{R}' + \text{MgX}_2$
4. $\text{R}_3\text{PO} + \text{R}'\text{M} \longrightarrow \text{R}_2\text{P}(\text{O})\text{R}' + \text{RM}$
5. $\text{R}_3\text{PO} + 2\text{M} \longrightarrow \text{R}_2\text{P}(\text{O})\text{M} \xrightarrow{\text{R}'\text{X}} \text{R}_2\text{P}(\text{O})\text{R}'$
6. $\text{R}_3\text{PX}_2 + 2\text{H}_2\text{O} \longrightarrow \text{R}_3\text{P}(\text{OH})_2 \longrightarrow \text{R}_3\text{PO}$
7. $\text{R}_2\text{POR}' + \text{R}''\text{X} \longrightarrow [\text{R}_2\text{P}(\text{OR}')\text{R}'']\text{X} \longrightarrow \text{R}_2\text{R}''\text{PO}$

8. $R_3P^+R' \cdot OH^- \xrightarrow{d} R_3PO + R'H$
9. $R_2PNR_2 + R'X \longrightarrow R_2P^+R'(NR_2) \cdot X^-$
 $\xrightarrow{OH^-} R_2P(O)R'$
10. $R_3P \xrightarrow{[OX]} R_3PO$
11. $R_2POR \xrightarrow{d} R_3PO$
12. $R_2P(O)CH_2CH_2Cl \xrightarrow{-HCl} R_2P(O)CH=CH_2$
13. その他

方法 IIIb

1. $R_2'P(S)X + R''MgX \longrightarrow R_2'P(S)R'' + MgX_2$
2. $PSX_3 + 3RM \longrightarrow R_3P=S + 3MX$
3. $R_3P + S \longrightarrow R_3P=S$
4. $R_3P \cdot HgCl_2 \xrightarrow{(NH_4)_2S_x} R_3P=S$

方法 IIIc

1. $R_3P=O \xrightarrow{\text{ハロゲン化試剤}} R_3PX_2$
2. $R_3P + X_2 \longrightarrow R_3PX_2$
3. $R_3P \xrightarrow{\text{ハロゲン化試剤}} R_3PX_2$
4. その他

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IV Phosphinous halides (R_2PX), phosphinites (R_2POR), trihalogenophosphoranes (R_2PX_3), phosphinic halides ($R_2P(Z)X$), phosphinic acids and their esters ($R_2P(Z)ZH$, $R_2P(Z)ZR$), dipphosphines and their dioxides and disulfides (R_2PPR_2 , $R_2P(Z)P(Z)R_2$), cyclophosphines (RP) $_n$, phosphinic anhydrides ($(R_2P(O))_2O$)

分子式	構造式	化合物名	方法	収率	文献	物理定数
C_2H_5BrP	Me_2PBr	Dimethylphosphinous bromide	2	50	33	93~95(100~105/716)
C_2H_5ClP	Me_2PCl	Dimethylphosphinous chloride	8	97	48a	(77~9/756) n_D^{20} 1.542
			3	60	3	(70/690) d_4^{20} 1.2625 d^{23} 1.2281
C_3H_5ClP	$MeEtPCl$	Ethylmethylphosphinous chloride	5	68.3	57	(49~57/15)(157~160) n_D^{20} 1.474
$C_4H_{10}ClP$	Et_2PCl	Diethylphosphinous chloride	5	66	57	(60~70/15)(61~2/72) d^{20} 1.0467
			8	75.5	11	n_D^{20} 1.472 d^{20} 1.0233
			2	70	50	
$C_4H_{11}OP$	$MeEtPOMe$	Methyl ethylmethylphosphinite	14	68	81	(87.5~88.5/7) n_D^{20} 1.4485
						d^{20} 1.0043
$C_6H_{14}ClP$	$i-Pr_2PCl$	Diisopropylphosphinous chloride	13	60	93	46~7/10 n_D^{20} 1.4752
$C_6H_{15}OP$	Et_2POEt	Ethyl diethylphosphinite	16	31	15	(84~5/15) n_D^{20} 1.4328
						d^{20} 0.9964
			17		31	
$C_6H_{10}ClP$	$EtPhPCl$	Ethylphenylphosphinous chloride	2	73	67	(180~90/15) (76/2) n_D^{20} 1.5707
$C_8H_{18}ClP$	Bu_2PCl	Dibutylphosphinous chloride	7	89	61	(91~2/12) (77~81/1)
			8	85.5	11	
$C_8H_{19}OP$	Pr_2POEt	Ethyl dipropylphosphinite	17		87	(97~103/15)
$C_8H_{19}OP$	$EtBuPOEt$	Ethyl butylethylphosphinite	18	47	25	(63~4/15) n_D^{20} 1.4428
$C_9H_{19}OP$	$MePhPOEt$	Ethyl methylphenylphosphinite	17		87	(125~30/15)
$C_{10}H_{19}OP$	$EtPhPOEt$	Ethyl ethylphenylphosphinite	15	54	25	(101~2/14) n_D^{20} 1.5268
						d^{20} 1.0750
$C_{10}H_{23}OP$	Bu_2POEt	Ethyl dibutylphosphinite	16	63	25	(99~100/17) n_D^{20} 1.4487
$C_{12}H_{10}ClP$	Ph_2PCl	Diphenylphosphinous chloride	9	70	17	(316~20)(170~71/10)
						n_D^{20} 1.6340 d_4^{20} 1.1801
$C_{12}H_{17}OP$	$(CH_2=CH)Ph$ $POBu$	Butyl phenylvinylphosphinite	18	66.5	84	(76~7/2) n_D^{20} 1.5310 d^{20} 0.9762
$C_{13}H_{19}OP$	Ph_2POMe	Methyl diphenylphosphinite	14	70	81	(151~2/10) n_D^{20} 1.6030
						d_0^{15} 1.1040
$C_{14}H_{19}OP$	Ph_2POEt	Ethyl diphenylphosphinite	17	87	60	(127~8/1) n_D^{20} 1.5910 d^0 1.0896
$C_{18}H_{19}OP$	Ph_2POPh	Phenyl diphenylphosphinite	16	42	15	(167~70/2) n_D^{20} 1.6331
$C_{20}H_{19}OP$	$(PhCH_2)_2POPh$	Phenyl dibenzylphosphinite	16	15	15	(200~3/2.5)
$C_2H_5F_3P$	Me_2PF_3	Trifluorodimethylphosphorane	19	81	90	(61~62/745) n_D^{20} 1.3230
						d^{20} 1.2155
$C_4H_{10}Cl_3P$	Et_2PCl_3	Trichlorodiethylphosphorane	19	80	2	65(dec)

分子式	构造式	化 合 物 名	方法	收 率	文献	物 理 定 数
C ₄ H ₁₀ Br ₃ P	Et ₂ PBr ₃	Tribromodiethylphosphorane	19	78	2	103.5
C ₄ H ₁₀ F ₃ P	Et ₂ PF ₃	Trifluorodiethylphosphorane	20	62.8	29	(50/100) (104~105/763) n_D^{20} 1.3650 d_4^{20} 1.1486
C ₁₂ H ₁₀ F ₃ P	Ph ₂ PF ₃	Trifluorodiphenylphosphorane	21	42	45	(91~4/0.5) (106~7/2)
			20	72	88	
C ₁₂ H ₁₀ Cl ₃ P	Ph ₂ PCl ₃	Trichlorodiphenylphosphorane	22	97	42	194~200(dec)
			24	94	17	
			26	98	41	
C ₁₂ H ₁₀ I ₃ P	Ph ₂ PI ₃	Triiododiphenylphosphorane	23	95.5	13	
C ₂ H ₆ ClOP	Me ₂ P(O)Cl	Dimethylphosphinic chloride	31	80	44	68(204)
			32	90	63	
C ₂ H ₇ O ₂ P	Me ₂ P(O)OH	Dimethylphosphinic acid	27	95	6	88.5~90.5
C ₂ H ₇ S ₂ P	Me ₂ P(S)SH	Dimethylphosphinodithioic acid	43	22.4	85	47~50
C ₂ H ₆ ClSP	Me ₂ P(S)Cl	Dimethylphosphinothioic chloride	49	77.2	18	(72~75/12) n_D^{20} 1.5451
C ₃ H ₈ ClSP	MeEtP(O)Cl	Ethylmethylphosphinic chloride	32	88	19	(99~102/15) n_D^{20} 1.4702
C ₃ H ₈ ClSP	MeEtP(S)Cl	Ethylmethylphosphinothioic chloride	49	82	18	(90~91/11)
			50	83.2	76	n_D^{20} 1.531 d_4^{20} 1.1815
C ₃ H ₉ OSP	MeEtP(S)OH	Ethylmethylphosphinothioic acid	42	—	67	(73~9/0.06) n_D^{20} 1.5117
C ₃ H ₉ O ₂ P	MeEtP(O)OH	Ethylmethylphosphinic acid	27	81	18	(170~2/11) 7~8 n_D^{20} 1.4505
C ₃ H ₉ O ₂ P	Me ₂ P(O)OMe	Methyl dimethylphosphinate	34	78	6	(78.5~9.5) n_D^{20} 1.4299
C ₄ H ₁₀ ClOP	Et ₂ P(O)Cl	Diethylphosphinic chloride	31	86	52	(79~81/15) (108~9.5/16)
			32	78	63	n_D^{20} 1.4647 d_4^{20} 1.1394
C ₄ H ₁₀ ClSP	Et ₂ P(S)Cl	Diethylphosphinothioic chloride	50	84.6	76	(117~20/15) (90~90.5/8)
			49	88	18	n_D^{20} 1.5294 d_4^{20} 1.1438
			48	84.3	79	
C ₄ H ₁₁ OSP	Et ₂ P(S)OH	Diethylphosphinothioic acid	39	78	54a	11.5(67~8/0.12)
			41	69	77	(88.5~9/1.5) n_D^{20} 1.5257
C ₄ H ₁₁ O ₂ P	Et ₂ P(O)OH	Diethylphosphinic acid	27	76	24	(197/22)
C ₄ H ₁₁ S ₂ P	Et ₂ P(S)SH	Diethylphosphinodithioic acid	43	72.5	79	(68.5~9/2.5) n_D^{20} 1.5858
C ₅ H ₁₃ O ₂ P	Et ₂ P(O)OMe	Methyl diethylphosphinate	34	65	30	d_4^{20} 1.1306 (86/12)
			38	80	75	n_D^{20} 1.4392 d_4^{20} 1.0261
C ₆ H ₁₄ ClOP	Pr ₂ P(O)Cl	Dipropylphosphinic chloride	31	78	39	(112~4/15) n_D^{20} 1.4638
			31	81	77	(110.5~2/8) d_4^{20} 1.0692
C ₆ H ₁₃ O ₂ P	Pr ₂ P(O)OH	Dipropylphosphinic acid	27	72	24	59.5
C ₆ H ₁₃ O ₂ P	Et ₂ P(O)OEt	Ethyl diethylphosphinate	38	80	75	(91~2/14) n_D^{20} 1.4337
						d_4^{20} 0.9964
C ₆ H ₁₃ S ₂ P	<i>i</i> -Pr ₂ P(S)SH	Diisopropylphosphinodithioic acid	43	89.2	79	(76~6.5/3) n_D^{20} 1.5745 d_4^{20} 1.0877
C ₆ H ₁₃ S ₂ P	Pr ₂ P(S)SH	Dipropylphosphinodithioic acid	43	69.4	79	(91~91.5/2) n_D^{20} 1.5632
						d_4^{20} 1.0691
C ₇ H ₈ ClOP	MePhP(O)Cl	Methylphenylphosphinic chloride	32	89	19	(167/22) (124~8/0.6)
			31	94	49	36~8 n_D^{20} 1.5602
C ₇ H ₈ ClSP	MePhP(S)Cl	Methylphenylphosphinothioic chloride	49	88.5	18	
C ₇ H ₉ O ₂ P	MePhP(O)OH	Methylphenylphosphinic acid	27	79.5	43	133~4
			30	80	4	
C ₇ H ₉ S ₂ P	MePhP(S)SH	Methylphenylphosphinodithioic acid	47	75	62	n_D^{20} 1.6787

分子式	構造式	化合物名	方法	収率	文献	物理定数
C ₇ H ₁₇ OSP	Pr ₂ P(S)OCH ₃	O-Methyl dipropylphosphinothioate	52	60.5	2	(118~9/12)
C ₈ H ₁₈ ClOP	Bu ₂ P(O)Cl	Dibutylphosphinic chloride	31	92	52	(156~7/28) (142~4/11)
			32	70	63	n_D^{20} 1.4643 d_4^{20} 1.0296
C ₈ H ₁₉ OSP	Bu ₂ P(S)OH	Dibutylphosphinothioic acid	39	85	64	(81~1.5/0.025)
C ₈ H ₁₉ O ₂ P	Bu ₂ P(O)OH	Dibutylphosphinic acid	27	71.5	24	(208~210/3) 71
			29	87	52	
C ₈ H ₁₉ O ₂ P	Pr ₂ P(O)OEt	Ethyl dipropylphosphinate	34	80	39	(110~2/14) n_D^{21} 1.4369
						d_4^{21} 0.9567
C ₈ H ₁₉ S ₂ P	Bu ₂ P(S)SH	Dibutylphosphinodithioate	43	78	79	(99~9.5/2)
			44	91	59	n_D^{20} 1.5481 d_4^{20} 1.0314
C ₈ H ₁₉ S ₂ P	<i>i</i> -Bu ₂ P(S)SH	Diisobutylphosphinodithioic acid	44	84	64	39~40
C ₁₆ H ₁₅ S ₂ P	Et ₂ P(S)SPh	Phenyl diethylphosphinodithioate	55	13.6	5	(128.5~30/0.02) n_D^{20} 1.6211
						d_4^{20} 1.1387
C ₁₀ H ₂₃ O ₂ P	Bu ₂ P(O)OEt	Ethyl dibutylphosphinate	34	74	39	(96/1.2) n_D^{22} 1.4421 d_4^{22} 0.9349
C ₁₂ H ₁₀ ClOP	Ph ₂ P(O)Cl	Diphenylphosphinic chloride	31	81	41	(222/16) (160~2/0.15) n_D^{23} 1.6068
C ₁₂ H ₁₀ ClSP	Ph ₂ P(S)Cl	Diphenylphosphinothioic chloride	48	75	41	(275~8/15) (155~60/0.13)
			51	90	34	
C ₁₂ H ₁₁ O ₂ P	Ph ₂ P(O)OH	Diphenylphosphinic acid	28	96	89	194~5
C ₁₂ H ₁₁ S ₂ P	Ph ₂ P(S)SH	Diphenylphosphinodithioic acid	47	89	62	55~6
			46	80	41	
C ₁₂ H ₂₃ S ₂ P	(<i>c</i> -C ₆ H ₁₁) ₂ P(S)SH	Dicyclohexylphosphinodithioic acid	44	90	59	103~105
C ₁₃ H ₂₆ O ₂ P	(<i>c</i> -C ₆ H ₁₁) ₂ P(O)OMe	Methyl dicyclohexylphosphinate	36	75.5	70	58~9
C ₁₄ H ₁₅ OSP	(PhCH ₂) ₂ P(S)OH	Dibenzylphosphinothioic acid	41	72	77	171
C ₁₄ H ₁₅ O ₂ P	Ph ₂ P(O)OEt	Ethyl diphenylphosphinate	52	30	38	(195~8/0.5)
C ₁₄ H ₁₅ O ₂ P	(PhCH ₂) ₂ P(O)OH	Dibenzylphosphinic acid	29	63.5	48a	191~2
C ₁₄ H ₁₅ S ₂ P	(PhCH ₂) ₂ P(S)SH	Dibenzylphosphinodithioic acid	43	93.2	79	132.5~133.5
C ₁₄ H ₁₇ N ₂ OP	Ph ₂ P(O)NHNMe ₂	(2, 2-Dimethylhydrazino) diphenylphosphine oxide	58		91	167~8
C ₁₄ H ₁₇ N ₂ SP	Ph ₂ P(S)NHNMe ₂	(2, 2-Dimethylhydrazino) diphenylphosphine sulfide	58		91	95.5~7
C ₄ H ₁₂ P ₂	Me ₂ PPMe ₂	Tetramethyldiphosphine	59	90	23, 56	(140.2) -2.25
			60	85	46	
			61	81	46	
			62	96	46	
C ₄ H ₁₁ S ₂ P ₂	Me ₂ P(S)P(S)Me ₂	Tetramethyldiphosphine disulfide	67	74	94	227
C ₆ H ₁₆ P ₂	MeEtPPMeEt	1, 2-Diethyl-1, 2-dimethyldiphosphine	59	65.4	56	(188~190)
C ₈ H ₂₀ P ₂	Et ₂ PPEt ₂	Tetraethyldiphosphine	63	91	11	(220~1)
			65	81	12	
			59	80	23	
C ₈ H ₂₀ S ₂ P ₂	Et ₂ P(S)P(S)Et ₂	Tetraethyldiphosphine disulfide	67	96	23	77~8
C ₁₂ H ₂₈ P ₂	Pr ₂ PPPr ₂	Tetrapropyldiphosphine	59	79.6	23	(112~3/5)
					2	
C ₁₄ H ₁₆ P ₂	MePhPPMePh	1, 2-Dimethyl-1, 2-diphenyldiphosphine	66	83	58	(128~30/0.5) 75~7
					56	
C ₁₆ H ₃₆ P ₂	Bu ₂ PPBu ₂	Tetrabutylidiphosphine	63	77.8	23	(180~2/14)

分子式	構造式	化合物名	方法	収率	文献	物理定数
$C_{16}H_{28}S_2P_2$	$Bu_2P(S)P(S)Bu_2$	Tetrabutylidiphosphine disulfide	59	70	23	
$C_{24}H_{20}P_2$	Ph_2PPH_2	Tetraphenyldiphosphine	67	70	23	74.5~75
			61	80	7	(258~60/1) 120.5
			59	90	23	
$C_{24}H_{20}S_2P_2$	$Ph_2P(S)P(S)Ph_2$	Tetraphenyldiphosphine disulfide	68	79	23	168~9
$C_{24}H_{44}P_2$	$(C_6H_{11})_2P-P(C_6H_{11})_2$	Tetracyclohexyldiphosphine	63	67.7	11	172
			65	84	12	
$C_{28}H_{28}S_2P_2$	$(PhCH_2)_2P(S)P(S)(PhCH_2)_2$	Tetrabenzylidiphosphine disulfide	67	25.1	10	145~50
$C_8H_{20}P_4$	$(EtP)_4$	Tetrakisethylcyclotetraphosphine	71	81.1	72	(168~70)
$C_{10}H_{25}P_5$	$(EtP)_5$	Pentakisethylcyclopentaphosphine	72	58	74	149~50
$C_{24}H_{20}P_4$	$(PhP)_4$	Tetrakisphenylcyclotetraphosphine	71	90	9	150.5
			72	82	58	
$C_{30}H_{25}P_5$	$(PhP)_5$	Pentakisphenylcyclopentaphosphine	73	83	36	154~6
$C_{24}H_{44}P_4$	$(c-C_6H_{11}P)_4$	Tetrakis(cyclohexyl)cyclotetraphosphine	70	70	22	219~20
			71	79	71	
$C_8H_{20}O_3P_2$	$Et_2P(O)OP(O)Et_2$	Diethylphosphinic anhydride	75	73	27	(124~5/0.5)
			74	72	24	n_D^{20} 1.4727
$C_8H_{24}N_4O_3P_2$	$(Me_2N)_2P(O)OP(O)(NMe_2)_2$	Octamethylpyrophosphoramidate	73	94.5	92	(120~2/0.5) d_4^{25} 1.09
$C_{12}H_{28}O_3P_2$	$Pr_2P(O)OP(O)Pr_2$	Dipropylphosphinic anhydride	74	74	24	(133~4/0.5) 28~30
$C_{24}H_{20}O_3P_2$	$Ph_2P(O)OP(O)Ph_2$	Diphenylphosphinic anhydride	77	82	95	142~3

方 法

- Red P + RX $\xrightarrow{d}$ R_2PX
- $RPX_2 + R_4Pb \rightarrow R_2PX$
- $RPX_2 + RCl \xrightarrow{AlCl_3} R_2PX$
- $R_2P(S)X + Bu_3P \rightarrow R_2PX + Bu_3PS$
- $RR'PCl_3 \cdot AlCl_3 \xrightarrow{Al/KCl} RR'PCl$
- $P-Cu + RX \xrightarrow{d} R_2PX$
- $R_2PH + COX_2 \rightarrow R_2PX + CO + HX$
- $R_2P-NR_2' \xrightarrow{HX} R_2PX$
- $RPCl_2 \xrightarrow{AlCl_3} R_2PCl$
- $R_2PPR_2 + X_2 \rightarrow 2R_2PX$
- $R_2POH + SOCl_2 \rightarrow R_2PCl$
- $R_3PCl_2 \rightarrow R_2PCl + RCl$
- $RMgX + PCl_3 \rightarrow R_2PCl$
- $R_2POR'' + R'OH \xrightarrow{Na} R_2POR'$
- $RP(OR'')_2 + RPCl_2 + R'MgCl \rightarrow RR'P(OR'')$
- $(R'O)PCl_2 + 2RMgX \rightarrow R_2P(OR') + 2MgXCl$
- $R_2PX + R'OH \xrightarrow{Base} R_2P(OR')$
- $RP(OR'')X + R'MgX \rightarrow RR'P(OR'')$
- $R_2P(S)P(S)R_2 + X_2 \rightarrow R_2PX_3$
- $R_2PX + SbX_3 \text{ or } AsX_3 \rightarrow R_2PX_3$
- $R_2P(O)OH + SF_4 \rightarrow R_2PF_3$
- $R_2PX + X_2 \rightarrow R_2PX_3$
- $R_2PPR_2 + X_2 \rightarrow R_2PX_3$
- $R_2P(O)OH + PCl_3 \rightarrow R_2P(O)Cl \xrightarrow{PCl_3} R_2PCl_3$
- $RPCl_2 + R'Cl \xrightarrow{AlCl_3} RR'PCl_3 \cdot AlCl_3$
- $R_2P(S)SH + 3Cl_2 \rightarrow R_2PCl_3 + S_2Cl_2 + HCl$
- $R_2P(S)P(S)R_2 + H_2O_2 \text{ or } AgO \xrightarrow{H_2O} R_2P(O)OH$
- $R_2PCl + H_2O_2 \xrightarrow{H_2O} R_2P(O)OH$
- $R_2P(O)H \xrightarrow{[O]} R_2P(O)OH$
- $R_2P(O)R' + NaOH \rightarrow R_2P(O)ONa + R'H$
- $R_2P(O)OR \text{ or } R_2P(O)OH + PCl_3 \text{ or } SOCl_2 \rightarrow R_2P(O)Cl$
- $R_2P(S)P(S)R_2 + SOCl_2 \rightarrow R_2P(O)Cl$
- $R_2P(S)P(S)R_2 + 3SO_2Cl_2 \rightarrow 2R_2P(O)Cl + SO_2 + 2S + SOCl_2$

34. $R_2P(O)Cl + NaOR' \longrightarrow R_2P(O)OR' + NaCl$
35. $R_2P(O)OH + R'X \longrightarrow R_2P(O)OR' + HX$
36. $R_2P(O)OH + R'N_2 \longrightarrow R_2P(O)OR'H$
($R' = CH_2, CHCH_3$)
37. $R_2PCl_3 + 2R'OH \longrightarrow R_2P(O)OR' + 2HCl + R'Cl$
38. $RP(OR')_2 + R''X \longrightarrow RR''P(O)OR' + R'X$
39. $R_2P(S)Cl + H_2O \longrightarrow R_2P(S)OH$
40. $RMgBr + PSCl_3 \xrightarrow{H_2O} R_2P(S)OH$
41. $R_2P(O)Na + S \xrightarrow{H_2O} R_2P(O)SH$
42. $R_2P(O)Cl + NaSH \xrightarrow{H^+} R_2P(S)OH$
43. $R_2P(S)X + 2 NaHS \text{ (or } H_2S) \xrightarrow{CH_3ONa} R_2P(S)SH$
44. $R_2PH + S \longrightarrow R_2P(S)H \longrightarrow R_2P(S)SH$
45. $RMgBr + P_2S_5 \longrightarrow 2 R_2P(S)SMgBr \xrightarrow{HCl} 2 R_2P(S)SH$
46. $C_6H_6 + P_2S_5 \longrightarrow 2 Ph_2P(S)SH + H_2S$
47. $(RPS_2)_2 + C_6H_6 \xrightarrow{AlCl_3} RPhP(S)SH$
48. $R_2P(S)OH + PCl_5 \text{ or } SOCl_2 \longrightarrow R_2P(S)Cl$
49. $R_2P(S)P(S)R_2 + SO_2Cl_2 \longrightarrow R_2P(S)Cl + SO_2$
50. $R_2P(S)Cl + S \longrightarrow R_2P(S)Cl$
51. $ArH + PSCl_3 \xrightarrow{AlCl_3} Ar_2P(S)Cl$
52. $R_2P(S)Cl + NaOR' \longrightarrow R_2P(S)OR' + NaCl$
53. $R_2P(S)SH + HOR' \longrightarrow R_2P(S)OR' + H_2S$
54. $R_2POR' + S \longrightarrow R_2P(S)OR'$
55. $R_2P(S)SM + R'Cl \longrightarrow R_2P(S)SR'$
56. $R_2P(S)SH + R'OH \longrightarrow R_2P(S)SR' + H_2O$
57. $R_2P(S)Cl + HSR' \longrightarrow R_2P(S)SR'$
58. $R_2PNHNR_2 \xrightarrow{[O], S} R_2P(Z)NHNR_2 \text{ } Z=O, S$
59. $R_2P(S)P(S)R_2 + \text{metal or } Bu_3P \longrightarrow R_2PPR_2$
60. $R_2PH + R_2'NPR_2 \longrightarrow R_2PPR_2$
61. $R_2PH + R_2PCl \longrightarrow R_2PPR_2$
62. $R_2'NPR_2 + R_2PH \cdot HCl \longrightarrow R_2PPR_2$
63. $R_2PCl + Na \longrightarrow R_2PPR_2$
64. $R_2PX + MPR_2 \longrightarrow R_2PPR_2$
65. $R_2PLi + BrCH_2CH_2Br \longrightarrow R_2PPR_2$
66. $RNaPPNaR + R'Cl \longrightarrow RR'PRR'$
67. $RMgX + PSCl_3 \longrightarrow R_2P(S)P(S)R_2$
68. $R_2P(S)Cl + R_2P(S)H \longrightarrow R_2P(S)P(S)R_2$
69. $R_2P(S)Cl + R'MgX \longrightarrow R_2P(S)P(S)R_2$
70. $RHPK + Br_2 \longrightarrow (RP)_n$
71. $RPCL_2 + RPH_2 \longrightarrow (RP)_n$
72. $RPCL_2 + LiAlH_4, LiH, Na \text{ or } Li \longrightarrow (RP)_n$
73. $RP(NMe_2)_2 + RPH_2 \longrightarrow (RP)_n$
74. $R_2P(S)P(S)R_2 + HgO \longrightarrow R_2P(O)OP(O)R_2$
75. $R_2P(O)Cl + R_2'P(O)OR'' \longrightarrow R_2P(O)OP(O)R_2'$
76. $2R_2P(O)Cl + H_2O \xrightarrow{Et_3N} R_2P(O)OP(O)R_2$
77. $R_2P(O)Cl + R_2P(O)ONa \longrightarrow R_2P(O)OP(O)R_2$

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Va phosphonous dihalides (RPX₂), phosphonous acids and its esters (RP(OH)₂, RP(OR)₂)

分子式	構造式	化合物名	方法	収率	文献	物理定数
CH ₃ Cl ₂ P	MePCl ₂	Methylphosphonous dichloride	1	g	1	(77~79), (80~81/729)
			2	87	2	(81~82), n_D^{25} 1.4960
			6	90	3	d_{20} 1.3039
CH ₃ Br ₂ P	MePBr ₂	Methylphosphonous dibromide	1	97	1	(138.5/720), (139~140) -58, n_D^{20} 1.6104 d_{20} 2.186
C ₂ H ₅ O ₂ P	MeP(OEt) ₂	Diethyl methylphosphonite	9	82	4	(47/50) n_D^{25} 1.4168
C ₁₃ H ₁₃ O ₂ P	MeP(OPh) ₂	Diphenyl methylphosphonite	9	82	5	(105~106/1) n_D^{20} 1.5671 d_{20} 1.1420
C ₂ H ₅ Cl ₂ P	EtPCl ₂	Ethylphosphonous dichloride	2	80	2	(26/25), (112), (114~117)
			3	89~96	6,7	n_D^{20} 1.4938, d_{20} 1.2563
			6	86.3	8	
C ₂ H ₅ Br ₂ P	EtPBr ₂	Ethylphosphonous dibromide	1	95	1	(161)
			3	78	9	n_D^{15} 1.5451 d_{20}^{20} 1.8216
C ₂ H ₇ O ₂ P	EtP(OH) ₂	Ethylphosphonous acid	8		10	d_{19} 1.2952
C ₄ H ₁₁ O ₂ P	EtP(OMe) ₂	Dimethyl ethylphosphonite	9	30	11	(73.5~74.5/225) n_D^{20} 1.4210 d_{20} 0.9515
C ₆ H ₁₅ O ₂ P	EtP(OEt) ₂	Diethyl ethylphosphonite	9	64.3	11	(137~139)
			9	q	12	n_D^{20} 1.4222 d_{20}^{20} 0.9024
C ₁₄ H ₁₅ O ₂ P	EtP(OPh) ₂	Diphenyl ethylphosphonite	9	76	13	(113~115/1) n_D^{20} 1.5623 d_{20} 1.1000
C ₄ H ₁₀ ClOP	EtP(OEt)Cl	Ethyl ethylphosphonochloridite	11	77	14,15	(35~36/18) n_D^{20} 1.4554
C ₃ H ₇ Cl ₂ P	PrPCl ₂	Propylphosphonous dichloride	3	50.6	16	(43/15), (140~142) n_D^{20} 1.4842 d_{20} 1.1664
C ₃ H ₇ O ₂ P	PrP(OH) ₂	Propylphosphonous acid	8		10	d_{13} 1.1418
C ₇ H ₁₇ O ₂ P	PrP(OEt) ₂	Diethyl propylphosphonite	9	64	17	(52~53/12) n_D^{20} 1.4275 d_{20} 0.9029
C ₄ H ₉ Cl ₂ P	BuPCl ₂	Butylphosphonous dichloride	4	75	18	(74/33), (157~160) n_D^{20} 1.4880, 1.4838 d_{20} 1.1670, d_{20}^{20} 1.1341
C ₈ H ₁₉ O ₂ P	BuP(OEt) ₂	Diethyl butylphosphonite	9	64	17	(78/20) n_D^{20} 1.4310
C ₆ H ₅ Cl ₂ P	PhPCl ₂	Phenylphosphonous dichloride	5	72~78	19	(68~70/1), (90~92/10)
			5	90	20	(140~142/57), (221~222) n_D^{20} 1.5960, n_D^{25} 1.5962 d_{20} 1.319
C ₆ H ₅ O ₂ P	PhP(OH) ₂	Phenylphosphonous acid	8	91	21	82~84
C ₁₀ H ₁₅ O ₂ P	PhP(OEt) ₂	Diethyl phenylphosphonite	9	80	22	(63~65/1) n_D^{20} 1.5113 d_{20} 1.0235
C ₈ H ₁₁ O ₂ P	PhP(OMe) ₂	Dimethyl phenylphosphonite	9	70.6	23	(98/17), (105/20) n_D^{25} 1.5261 d_{20}^{24} 1.0732
C ₈ H ₁₀ ClOP	PhP(OEt)Cl	Ethyl phenylphosphonochloridite	11	74	14,15	(74~75/0.2) n_D^{20} 1.5664 d_{20} 1.2434
C ₇ H ₇ Cl ₂ P	PhCH ₂ PCl ₂	Benzylphosphonous dichloride	3	42	24	(118~119/12)
			1	20	25	n_D^{20} 1.586 d_{20} 1.300
C ₁₁ H ₁₇ O ₂ P	PhCH ₂ P(OEt) ₂	Diethyl benzylphosphonite	10	50	26	(88~90/3) n_D^{20} 1.5032
C ₁₆ H ₇ Cl ₂ P	1-C ₁₀ H ₇ PCl ₂	1-Naphthylphosphonous dichloride	3	25	27	(118~120/0.5), (180/10) 58~ 59, 54
C ₆ H ₅ Br ₂ P	PhPBr ₂	Phenylphosphonous dibromide	7	80	28	(259~261/1)

Vb phosphonic dihalides (RP(Z)X₂), phosphonic acids and their esters (RP(Z)(OH)₂, RP(Z)(OR)₂)

CH ₃ Cl ₂ OP	MeP(O)Cl ₂	Methylphosphonic dichloride	1	80	1	(53~54/10)
			1	90	43	32
			2	75~79	22, 3	n_D^{40} 1.4526 d_{20}^{40} 1.4382
			3	68	4	

分子式	構造式	化 合 物 名	方法	収 率	文献	物 理 定 数
$\text{CH}_5\text{O}_3\text{P}$	$\text{MeP}(\text{O})(\text{OH})_2$	Methylphosphonic acid	1	86	5, 6	
			19	63	7	105
			20		8	
$\text{C}_5\text{H}_{13}\text{O}_3\text{P}$	$\text{MeP}(\text{O})(\text{OEt})_2$	Diethyl methylphosphonate	23	83.5	9	(64~65/2), (90/10)
			27	95	10	$n_{\text{D}}^{25} 1.4119$
			30	g	11	$d_4^{25} 1.0508$
			24	80	12	
$\text{C}_7\text{H}_{17}\text{O}_3\text{P}$	$\text{MeP}(\text{O})(\text{OPr})_2$	Dipropyl methylphosphonate	24	66	12	(68~70/3), (105~106)
						$n_{\text{D}}^{18} 1.4082$ $d_4 1.0683$
$\text{C}_7\text{H}_{17}\text{O}_3\text{P}$	$\text{MeP}(\text{O})(\text{O-i-Pr})_2$	Diisopropyl methylphosphonate	40	85~90	13	(78~79/10)
			44	67.7	14	$n_{\text{D}}^{20} 1.4158$
			35	50	12	$d_4 0.9849$
$\text{C}_9\text{H}_{21}\text{O}_3\text{P}$	$\text{MeP}(\text{O})(\text{OBu})_2$	Dibutyl methylphosphonate	24	85	15	(132~135/15) $n_{\text{D}}^{20} 1.4246$
						$d_4^{20} 0.9770$
$\text{C}_{13}\text{H}_{15}\text{O}_3\text{P}$	$\text{MeP}(\text{O})(\text{OPh})_2$	Diphenyl methylphosphonate	27	91	16	(201~202/11), 36~37
			24	85	17	$n_{\text{D}}^{20} 1.5518$ $d_4^{20} 1.2051$
$\text{C}_5\text{H}_{13}\text{OPS}_2$	$\text{MeP}(\text{O})(\text{SEt})_2$	S,S-Diethyl methylphosphonodithioate	26	41.4	18	(135~138/16) $n_{\text{D}}^{20} 1.4523$
						$d_{20} 1.1412$
$\text{CH}_3\text{Cl}_2\text{PS}$	$\text{MeP}(\text{S})\text{Cl}_2$	Methylphosphonothioic dichloride	13	85	19	(69.5~70.5/50), (45~48/0.5)
			14	91.8	20	(142~143), (154)
			16	74	21	-25.8
			17	80	22	$n_{\text{D}}^{20} 1.5498$ $d_{20} 1.4220$
$\text{C}_3\text{H}_5\text{O}_2\text{PS}$	$\text{MeP}(\text{S})(\text{OMe})_2$	O,O-Dimethyl methylphosphonothioate	24	92	12	(52~52.5/8) $n_{\text{D}}^{20} 1.4743$
						$d_{20} 1.1435$
$\text{C}_{15}\text{H}_{13}\text{O}_2\text{PS}$	$\text{MeP}(\text{S})(\text{OEt})_2$	O,O-Diethyl methylphosphonothioate	24	90	12	(76.5~78/13)
			25	80	23	$n_{\text{D}}^{20} 1.4610$ $d_{20} 1.0553$
$\text{C}_7\text{H}_{17}\text{O}_2\text{PS}$	$\text{MeP}(\text{S})(\text{OPr})_2$	O,O-Dipropyl methylphosphonothioate	24	74.5	24	(95~96/8)
			25	77	23	$n_{\text{D}}^{20} 1.4626$ $d_{20} 1.0170$
$\text{C}_7\text{H}_{17}\text{O}_2\text{PS}$	$\text{MeP}(\text{S})(\text{Oi-Pr})_2$	O,O-Diisopropyl methylphosphonothioate	24	71	12	(42~44/0.25) $n_{\text{D}}^{20} 1.4508$
						$d_{20} 0.9926$
$\text{C}_9\text{H}_{21}\text{O}_2\text{PS}$	$\text{MeP}(\text{S})(\text{OPu})_2$	O,O-Dibutyl methylphosphonothioate	24	85.5	24	(93~94/0.7)
			14	87	25	$n_{\text{D}}^{20} 1.4535$ $d_{20} 0.9848$
			25	72	23	
$\text{C}_2\text{H}_5\text{Cl}_2\text{OP}$	$\text{EtP}(\text{O})\text{Cl}_2$	Ethylphosphonic dichloride	1	75	43	(75~78/50), (175)
			3	82	4	$n_{\text{D}}^{20} 1.4661$ $d_{20} 1.3678$
			4	70		
$\text{C}_2\text{H}_7\text{O}_3\text{P}$	$\text{EtP}(\text{O})(\text{OH})_2$	Ethylphosphonic acid	19	99	27	(330~340/8)
			19	75~85	28	61~62
$\text{C}_6\text{H}_{15}\text{O}_3\text{P}$	$\text{EtP}(\text{O})(\text{OEt})_2$	Diethyl ethylphosphonate	28	h	29	(82/10)
			31	77	30	$n_{\text{D}}^{20} 1.4168$ $d_4^{20} 1.0259$
			29	97	31	
			27	94	32	
$\text{C}_{10}\text{H}_{23}\text{O}_3\text{P}$	$\text{EtP}(\text{O})(\text{OBu})_2$	Dibutyl ethylphosphosphonate	31	78	33	(137~138/17) $n_{\text{D}}^{20} 1.4282$
						$d_4^{25} 0.9623$
$\text{C}_{14}\text{H}_{15}\text{O}_3\text{P}$	$\text{EtP}(\text{O})(\text{OPh})_2$	Diphenyl ethylphosphonate	27	80	34	(202/13)
			24	57	35	$n_{\text{D}}^{20} 1.5451$ $d_{20} 1.1799$
$\text{C}_2\text{H}_5\text{Cl}_2\text{PS}$	$\text{EtP}(\text{S})\text{Cl}_2$	Ethylphosphonothioic dichloride	16	82.5	36	(68~69/20), (82.5/48.5).

分子式	構造式	化 合 物 名	方法	収 率	文献	物 理 定 数
$C_6H_{15}O_2PS$	$EtP(S)(OEt)_2$	O, O-Diethyl ethylphosphonothioate	16	77	21	n_D^{20} 1.5435 d_{20} 1.3532
			14	90	37	
			17	44	22	
			24	75	20, 38	(78~78.5/8)
$C_{10}H_{23}O_2PS$	$EtP(S)(OBu)_2$	O, O-Dibutyl ethylphosphonothioate	14	74	39	n_D^{20} 1.4576 d_{20} 1.0349
			24	86	20	(79.5~83/2), (97~98/2)
			14	85	40	n_D^{20} 1.4533 d_{20} 0.9775
			31	61	41	
$C_3H_7Cl_2OP$	$PrP(O)Cl_2$	Propylphosphonic dichloride	1	75	42	(78/14), (88~90/50)
			1	75	43	n_D^{20} 1.4621, d 1.286
$C_3H_7Cl_2PS$	$PrP(S)Cl_2$	Propylphosphonothioic dichloride	13	53	19	(66~67/10), (88~90/50)
			17	60	22	n_D^{20} 1.5360 d_4^{20} 1.3005
$C_3H_9Cl_2OP$	$i-PrP(O)Cl_2$	Isopropylphosphonic dichloride	3	90	4, 44	(77~78/22), (82~84/50)
			1	70	43	n_D^{20} 1.4667 d_{20} 1.3001
$C_3H_9O_3P$	$i-PrP(O)(OH)_2$	Isopropylphosphonic acid	20		45	74~75
$C_7H_{17}O_3P$	$i-PrP(O)(OEt)_2$	Diethyl isopropylphosphonate	23	71	9	(56~58/18) n_D^{20} 1.4154
						n_D^{25} 1.4150 d_{20} 0.9951
$C_3H_7Cl_2PS$	$i-PrP(S)Cl_2$	Isopropylphosphonothioic dichloride	17	50	22	(70/12)
$C_4H_9Cl_2OP$	$BuP(O)Cl_2$	Butylphosphonic dichloride	1	75	43	(95.5~97/20), (96~97/17)
			5	45	46	n_D^{20} 1.4684(1.4670)
			8	40~66	47	d_{20} 1.2478(1.2492)
$C_4H_{11}O_3P$	$BuP(O)(OH)_2$	Buthylphosphonic acid	19	q	7, 48	105~106
$C_8H_{19}O_3P$	$BuP(O)(OEt)_2$	Diethyl buthylphosphonate	31	82	49	(74/1) n_D^{25} 1.4213
$C_4H_9Cl_2PS$	$BuP(S)Cl_2$	Buthylphosphonothioic dichloride	17	45	22	
$C_4H_9Cl_2OP$	$i-BuP(O)Cl_2$	Isobutylphosphonic dichloride	3	93	4, 50	(75~76/13)
			8	40~60	47	n_D^{20} 1.4645 d_{20} 1.2400
			19	60~70	7	125~126
$C_8H_{19}O_3P$	$i-BuP(O)(OEt)_2$	Diethyl isobutylphosphonate	32	77	51	(83/3)
			23	68	9	
$C_4H_9Cl_2PS$	$i-BuP(S)Cl_2$	Isobutylphosphonothioic dichloride	17	42	22	
$C_6H_5Cl_2OP$	$PhP(O)Cl_2$	Phenylphosphonic dichloride	9	90	52	(137~138/15), (258)
			1	94	53	n_D^{25} 1.5581 d_4^{25} 1.1970
			11	q	54	
$C_6H_7O_3P$	$PhP(O)(OH)_2$	Phenylphosphonic acid	3	31.5~78	55	
			20	75.2	56	165~166
			21	75.5	57	
$C_{10}H_{15}O_3P$	$PhP(O)(OEt)_2$	Diethyl phenylphosphonate	23	80.4	58	(121~123/2) n_D^{25} 1.4935
$C_{18}H_{15}O_3P$	$PhP(O)(OPh)_2$	Diphenyl phenylphosphonate	24	19.7	59, 60	
$C_{12}H_{15}O_3P$	$PhP(O)(OCH_2CH=CH_2)_2$	Diallyl phenylphosphonate	24	89.1	61	(128/1) n_D^{25} 1.4957 d_4^{25} 1.1097
$C_{16}H_{13}Cl_2O_3P$	$PhP(O)(OCH_2CH_2Cl)_2$	Bis(2-chloroethyl) phenylphosphonate	52	91	62	(170~172/2) n_D^{20} 1.5258
$C_6H_5Cl_2PS$	$PhP(S)Cl_2$	Phenylphosphonothioic dichloride	14	92	63	(122~123/10), (150/26)
			15	94	64	(205/125)
			18	83	65	n_D^{20} 1.6230 d_4^{20} 1.4050
			14	79.5	66	
$C_{10}H_{15}O_2PS$	$PhP(S)(OEt)_2$	O, O-Diethyl phenylphosphonothioate	24	66.6	67	(96/0.05), (163/20) n_D^{25} 1.5370 d_{15} 1.12

分 式 子	構 造 式	化 合 物 名	方法	収 率	文 献	物 理 定 数
$C_6H_{11}Cl_2OP$	$c-C_6H_{11}P(O)Cl_2$	Cyclohexylphosphonic dichloride	5	60~70	46	(90/1)(127.5~128.2)37.0~37.5 n_D^{20} 1.5059 d_{20} 1.2955
$C_6H_{13}O_3P$	$c-C_6H_{11}P(O)(OH)_2$	Cyclohexylphosphonic acid	22	86	68	166~167, 159
$C_{10}H_{21}O_3P$	$c-C_6H_{11}P(O)(OEt)_2$	Diethyl cyclohexylphosphonate	23	49	8	(148/1.5) n_D^{18} 1.4615 n_D^{25} 1.4538 d_{18}^{18} 1.032
$C_2H_3Cl_2OP$	$CH_2=CHP(O)Cl_2$	Vinylphosphonic dichloride	12	85.6	69	(67~69/21)
			12	89	70	n_D^{20} 1.4808 d_{20} 1.4092
			1	70	71	
$C_6H_{13}O_3P$	$CH_2=CHP(O)(OEt)_2$	Diethyl vinylphosphonate	12	95	72	(63/2.5) n_D^{20} 1.4300 d_{20} 1.0526
$C_7H_7Cl_2OP$	$PhCH_2P(O)Cl_2$	Benzylphosphonic dichloride	3	62	4, 44	(130/2)
			6	40		57.5
$C_7H_9O_3P$	$PhCH_2P(O)(OH)_2$	Benzylphosphonic acid	19	q	28	173~175, 168~169
$C_{11}H_{17}O_3P$	$PhCH_2P(O)(OEt)_2$	Diethyl benzylphosphonate	31	78	74	(155/14), (167~169/25) n_D^{20} 1.4965 d_4^{20} 1.1200
$C_{10}H_7Cl_2OP$	$2-C_{10}H_7P(O)Cl_2$	2-Naphthylphosphonic dichloride	1	60	75	(167~168/2) 45~47
$C_2H_3O_4P$	$CH_3COP(O)(OH)_2$	Acetylphosphonic acid	19	93.2	76	110~114
$C_6H_{13}O_4P$	$CH_3COP(O)(OEt)_2$	Diethyl acetylphosphonate	27	83	77	(70~73/2) n_D^{20} 1.4200 d_4^{20} 1.0991
$C_{11}H_{15}O_4P$	$PhCOP(O)(OEt)_2$	Diethyl benzoylphosphonate	27	66.5	78	(141/2.5) n_D^{20} 1.5065 d_4^{20} 1.1599
$C_5H_{11}Cl_2O_3P$	$Cl_2CHP(O)(OEt)_2$	Diethyl dichloromethylphosphonate	23	23	79	(82/0.2) n_D^{20} 1.4513
$C_5H_{13}ClO_3P$	$ClCH_2P(O)(OEt)_2$	Diethyl chloromethylphosphonate	24	91.5	80	(109~110/10) n_D^{20} 1.4424 d_{20} 1.1997
$C_5H_{13}O_4P$	$HOCH_2P(O)(OEt)_2$	Diethyl hydroxymethylphosphonate	33	30	81, 82	(72/5) (124~126/3) n_D^{20} 1.4342, 1.4322, d_4^{20} 1.0726, d_4^{20} 1.1396
$C_6H_{12}NO_3P$	$NCCH_2P(O)(OEt)_2$	Diethyl cyanomethylphosphonate	27	79	83, 84	(101~102/0.4), (120~121/1.5) n_D^{20} 1.4330 d_{20} 1.1264
			34	72	85	
$C_5H_{12}BrO_3P$	$BrCH_2P(O)(OEt)_2$	Diethyl bromomethylphosphonate	24	50	80	(99/1) n_D^{20} 1.4585 d_{20}^{20} 1.4474
$C_6H_{14}ClO_3P$	$ClCH_2CH_2P(O)(OEt)_2$	Diethyl 2-chloroethylphosphonate	24	60	86	(92~94/4), (103~110/7) n_D^{20} 1.4390, 1.4281 d_4^{20} 1.1565, d_4^{20} 1.1558
$C_7H_{15}O_5P$	$EtO_2CP(O)(OEt)_2$	Diethyl carbethoxyphosphonate	31	55	87	(135.3/12) n_D^{20} 1.4229 d_4^{20} 1.0450
$C_7H_{16}ClO_3P$	$Cl(CH_2)_3P(O)(OEt)_2$	Diethyl 3-chloropropylphosphonate	31	68	88	(90~91/1) n_D^{20} 1.4468 d_{20} 1.1399
CCl_5OP	$Cl_3CP(O)Cl_2$	Trichloromethylphosphonic dichloride	3	85	4, 44	155~156
					89	
CH_2Cl_3PS	$ClCH_2P(S)Cl_2$	Chloromethylphosphonothioic dichloride	13	66~72	90	
$C_3H_8ClO_2P$	$MeP(O)(OEt)Cl$	Ethyl methylphosphonochloride	35	88	91	(33/0.9), (83/21), n_D^{18} 1.4385, n_D^{25} 1.4320 d_4^{16} 1.2095
$C_2H_7O_3P$	$MeP(O)(OMe)(OH)$	Methyl hydrogen methylphosphonate	38	75	92	(104~105/0.1), (121~123/1) n_D^{20} 1.4245, 1.4222 d_{20} 1.3073
$C_4H_{11}O_3P$	$MeP(O)(OMe)(OEt)$	Ethyl methyl methylphosphonate	27	98	93	(74~75/15)
$C_3H_{13}O_2PS$	$MeP(O)(OEt)(SEt)$	O, S-Diethylphosphonothioate	43	59	94	(62~64/1), (90/12) n_D^{20} 1.4743, 1.4760 d_{20} 1.0940, 1.0969
$C_7H_{18}NO_2P$	$MeP(O)(OEt)(NEt_2)$	Ethyl N, N-diethyl-P-methylphosphonamidate	49	64	95, 96	(110~114/22)
$C_7H_{18}NOPS$	$MeP(O)(SEt)(NEt_2)$	S-Ethyl N, N-diethyl-P-methylphosphonamidothioate	50	31	97	(90~91/4) n_D^{20} 1.5032 d_{20} 1.1996

分子式	構造式	化合物名	方法	収率	文献	物理定数
C ₂ H ₇ O ₂ PS	MeP(S)(OMe)(OH)	O-Methyl hydrogen methylphosphonothioate	39	71	98	(75~83/0.3~0.5)
			40	41	99	n_D^{25} 1.5005 d_{20} 1.3015
C ₇ H ₁₈ NOPS	MeP(S)(OEt)(NEt)	O-Ethyl N, N-diethyl-P-methylphosphonamidothioate	14	64	100	(98~101/10) n_D^{20} 1.4828 d_{20} 1.0103
C ₃ H ₉ OPS ₂	MeP(S)(OEt)(SH)	O-Ethyl methylphosphonodithioate	45	87	101	(32/0.05)
					102	$n_D^{22.5}$ 1.5440
C ₄ H ₁₀ ClO ₂ P	EtP(O)(OEt)Cl	Ethyl ethylphosphonochloridate	35	80	103	(49~50/3)
			37	62	104	n_D^{25} 1.4345
			36	75	105	
C ₅ H ₁₃ O ₂ PS	EtP(O)(SMe)(OEt)	O-Ethyl S-methyl ethylphosphonothioate	44		106	(93.2/9) n_D^{20} 1.4790 d_{20} 1.1058
C ₂ H ₇ OPS ₂	EtP(S)(OH)(SH)	Ethylphosphonodithioic acid	46		107	
C ₈ H ₂₀ NOPS	EtP(S)(OEt ₂)NEt ₂	O-Ethyl triethylphosphonamidothioate	14	73	108	(115~116/9) n_D^{20} 1.4828 d_{20} 1.0042
C ₄ H ₁₁ OPS ₂	EtP(S)(OEt)(SH)	O-Ethyl ethylphosphonodithioate	45	q	102	(38/0.01) $n_D^{22.5}$ 1.5389
C ₄ H ₁₁ O ₂ PS	EtP(S)(OEt)(OH)	O-Ethyl hydrogen ethylphosphonothioate	41	75	109	(84.5~85.5/2)
			38	74	110	n_D^{20} 1.4916 d_{20} 1.1337
C ₅ H ₁₃ O ₂ PS	EtP(S)(OEt)(OMe)	O-Ethyl O-methyl ethylphosphonethioate	27	73	111	(74~75/9.5) n_D^{20} 1.4665 d_{20} 1.0647
C ₈ H ₁₀ ClO ₂ P	PhP(O)(OEt)Cl	Ethyl phenylphosphonochloridate	35	98	112	(120/2) n_D^{20} 1.5372, 1.5091
C ₈ H ₁₁ O ₃ P	PhP(O)(OEt)(OH)	Ethyl hydrogen phenylphosphonate	38	96	113	n_D^{20} 1.5258 d_{20} 1.2331
			48	84	114	
C ₈ H ₁₂ NO ₂ P	PhP(O)(OEt)(NH ₂)	Ethyl P-phenylphosphonamide	51	90.1	115	127
C ₈ H ₁₁ OPS ₂	PhP(S)(OEt)(SH)	O-Ethyl phenylphosphonodithioate	45	99	102	(83~85/0.03) n_D^{20} 1.6020 d_{20} 1.2310
C ₁₄ H ₁₅ OPS ₂	PhP(S)(OEt)(SPh)	O-Ethyl S-phenyl phenylphosphonodithioate	47	11.3	116	(125.5~126.5/0.25) n_D^{20} 1.6305 d_{20} 1.1749

Vc tetrahalogenophosphoranes (RPX₄)

CH ₃ Cl ₄ P	MePCl ₄	Tetrachloromethylphosphorane	5	~100	1	198~199
			2		2	
CH ₂ ClF ₄ P	ClCH ₂ PF ₄	Chloromethyltetrafluorophosphorane	3	75~82	3	(47)
CCl ₃ P	CCl ₃ PCl ₄	Tetrachlorotrichloromethylphosphorane	7	~100	4	125~126(dec)
			6	—	5	
			2	—	6	
C ₂ H ₅ Cl ₄ P	EtPCl ₄	Tetrachloroethylphosphorane	2	—	7	135(dec)
C ₂ H ₅ Br ₄ P	EtPBr ₄	Tetrabromoethylphosphorane	8	—	8	188~190
C ₂ H ₅ I ₄ P	EtPI ₄	Tetraiodoethylphosphorane	8	—	8	112~116
C ₆ H ₅ F ₄ P	PhPF ₄	Tetrafluorophenylphosphorane	9	66.7	9	(134.5~136)
			1	62	10	n_D^{20} 1.4245 d_{15}^{15} 1.3888
C ₆ H ₅ Cl ₄ P	PhPCl ₄	Tetrachlorophenylphosphorane	2	—	11	73
C ₆ H ₅ Br ₄ P	PhPBr ₄	Tetrabromophenylphosphorane	2	—	12	subl
C ₆ H ₅ Br ₂ Cl ₂ P	PhPBr ₂ Cl ₂	Dibromodichlorophenylphosphorane	2	—	13	208
C ₈ H ₇ Cl ₄ P	PhCH=CHPCl ₄	Tetrachlorostyrylphosphorane	4	90	14	65~68
C ₁₀ H ₇ Cl ₄ P	α -C ₁₀ H ₇ PCl ₄	Tetrachloro- α -naphtylphosphorane	2	—	15	143

方法 Va

1. $RX + P(\text{red or white}) \longrightarrow RPX_2$
2. $RCI + PCl_3 + AlCl_3 \longrightarrow \text{complex}$
 $\xrightarrow{Al} \xrightarrow{NaCl} RPCI_2$
3. $PX_3 + RM \longrightarrow RPX_2$
4. $PX_3 + RP(OR')_2 \longrightarrow RPX_2$
5. $PhH + PCl_3 + AlCl_3 \xrightarrow[\text{or } C_6H_5N]{POCl_3} PhPCl_2$
6. $RP(S)Cl_2 + R'_3P \text{ or } R'PCl_2 \longrightarrow RPCI_2$
7. $PhPCl_2 + HBr \xrightarrow{PBr_3} PhPBr_2$
8. $RPX_2 + H_2O \longrightarrow RP(OH)_2$
9. $RPX_2 + R'OH \longrightarrow RP(OR')_2$
 $X = \text{halogen or } NR_2''$
10. $(EtO)_2PCl + RMgCl \longrightarrow RP(OEt)_2$
11. $RP(OEt)_2 + RPCI_2 \longrightarrow RP(OEt)Cl$

方法 Vb

1. $RP(O)(OR')_2 + PCl_3, PCl_5$
 $\text{or } SOCl_2 \longrightarrow RP(O)Cl_2$
2. $HP(O)(OR)_2 \xrightarrow{d} \xrightarrow[\text{or } SOCl_2]{PCl_5} RP(O)Cl_2$
3. $RCI + PCl_2 + AlCl_3 \longrightarrow \text{complex} \xrightarrow{H_2O} RP(O)Cl_2$
4. $PCl_3 + R_4Pb \xrightarrow{O_2} RP(O)Cl_2$
5. $RH + PCl_3 \xrightarrow{O_2} RP(O)Cl_2$
6. $PhCHO + PCl_3 \xrightarrow{I_2} PhCH_2P(O)Cl_2$
7. $RPCI_2 + O_2 \longrightarrow RP(O)Cl_2$
8. $RPCI_2 + Cl_2 \xrightarrow{HCO_2H} RP(O)Cl_2$
9. $RPCI_2 + SO_2 + Cl_2 \longrightarrow RP(O)Cl_2$
10. $RPCI_2 + P_2O_5 + Cl_2 \longrightarrow RP(O)Cl_2$
11. $RPCI_2 + SO_3 \longrightarrow RP(O)Cl_2$
12. $ClCH_2CH_2P(O)Cl_2 + BaCl_2 \longrightarrow CH_2=CHP(O)Cl_2$
13. $RP(O)Cl_2 + P_2S_5 \text{ or } S \longrightarrow RP(S)Cl_2$
14. $RPX_2 + S \text{ or } PSCl_3 \longrightarrow RP(S)X_2$
 $X = Cl, OR', NR_2''$
15. $RPCI_4 + H_2S \longrightarrow RP(S)Cl_2$
16. $RCI + PCl_3 + AlCl_3 \xrightarrow[\text{or } Al, S, NaCl]{KCl, EtSH} RP(S)Cl_2$
17. $RSH + PCl_3 \longrightarrow RP(S)Cl_2$
18. $RH + AlCl_3 + PCl_3 \xrightarrow{Cl_2} \xrightarrow{H_2S} RP(S)Cl_2$
19. $RP(O)(OR')_2 + HX(\text{or heat}) \longrightarrow RP(O)(OH)_2$
20. $RP(O)Cl_2 + H_2O \longrightarrow RP(O)(OH)_2$
21. $PhH + P_4H_{10} \longrightarrow PhP(O)(OH)_2$
22. $PhP(O)(OH)_2 + H_2(Rh) \longrightarrow c-C_6H_{11}P(O)(OH)_2$

23. $RCI + PCl_3 + AlCl_3 \longrightarrow \text{complex}$
 $\xrightarrow{R'OH} RP(O)(OR')_2$
24. $RP(Z)X_2 + R'OH \longrightarrow RP(Z)(OR')_2$
 $X = \text{halogen or } NR_2''$
 $Z = O, S$
25. $RPCI_2 + S + R'OH \longrightarrow RP(S)(OR')_2$
26. $RP(O)Cl_2 + Et_2S_2 \xrightarrow{Na} RP(O)(SEt)_2$
27. $P(OR')_3 + RX \longrightarrow RP(O)(OR')_2$
28. $P(OR)_3 + CHCl_3 \longrightarrow RP(O)(OR)_2$
29. $P(OR)_3 + NaI \longrightarrow RP(O)(OR)_2$
30. $BrCH_2P(O)(OR)_2 + H_2(Pd) \longrightarrow CH_3P(O)(OR)_2$
31. $NaP(Z)(OR')_2 + \text{alkylating agents}$
 $\longrightarrow RP(Z)(OR')_2 \quad Z = O, S$
32. $HP(O)(OR)_2 + CH_3CH=CHCH_3 \longrightarrow i-BuP(O)(OR)_2$
33. $HP(O)(OEt)_2 + (CH_2O)_n \xrightarrow{Na} HOCH_2P(O)(OEt)_2$
34. $ClC \equiv CP(O)(Et)_2 + NH_3 \longrightarrow NCCH_2P(O)(OEt)_2$
35. $RP(O)(OR')_2 + SOCl_2, PCl_5,$
 $(COCl)_2 \text{ or } COCl_2 \longrightarrow RP(O)Cl(OR')$
36. $RP(O)(OR')SH + COCl_2 \longrightarrow RP(O)(OR')Cl$
37. $RCI + PCl_3 + AlCl_3 \xrightarrow{R'OH} RP(O)(OR')Cl$
38. $RP(Z)(OR')_2 \xrightarrow{OH^-} RP(Z)(OR')(OH)$
39. $RP(S)Cl_2 + R'OH + KOH \longrightarrow RP(S)(OR')(OH)$
40. $RP(O)Cl_2 + H_2S + R'OH \xrightarrow{Na} RP(S)(OR')(OH)$
41. $RP(S)(OR')Cl \xrightarrow{KOH} \xrightarrow{H_2SO_4} RP(S)(OR')(OH)$
42. $RP(S)(OR')Cl + R''OH \longrightarrow RP(S)(OR')(OR'')$
43. $RP(S)(OR')(ONa) + R''Br \xrightarrow{R''OH} RP(O)(OR')(SR'')$
44. $RP(S)(OR')OH + CH_2N_2 \longrightarrow RP(O)(OR')(SMe)$
45. $(RPS_2)_2 + R'OH \longrightarrow RP(S)(OR')(SH)$
46. $RMgBr + P_2S_5 \xrightarrow{NiSO_4} \xrightarrow[\text{H}^+]{(NH_4)_2S} RP(S)(OH)(SH)$
47. $PhP(S)(OR)SM + ClN_2Ph \longrightarrow PhP(S)(OR)(SPh)$
48. $(PhPO_2)_n + ROH \xrightarrow[\text{or } Ba(OH)_2]{Ca(OH)_2} [PhP(O)(OR)O]_2Ca \text{ or } Ba$
49. $RP(O)(OR')Cl + HN(R_2)'' \longrightarrow RP(O)(OR')(NR_2'')$

50. $\text{RPhCl}_2 + \text{R}_2''\text{NSR}' \xrightarrow{\text{SO}_2} \text{RP(O)(SR') (NR}_2'')$
 51. $\text{PhP(O)(NH}_2)_2 + \text{ROH} \longrightarrow \text{PhP(O)(OR)NH}_2$
 52. $\text{PhP(O)Cl}_2 + \text{PhSnCl}_3 + \text{CH}_2=\text{CH}_2$
 $\xrightarrow{\text{O}'} \longrightarrow \text{PhP(O)(OCH}_2\text{CH}_2\text{Cl)}_2$

方法 Vc

1. $\text{RP(O)F}_2 + \text{SF}_4 \longrightarrow \text{RPF}_4 + \text{SOF}_2$
2. $\text{RPX}_2 + \text{Y}_2 \longrightarrow \text{RPX}_2\text{Y}_2$
3. $3 \text{RPX}_2 + 3 \text{SbF}_3 \longrightarrow 3 \text{RPF}_4 + 2 \text{SbX}_3 + \text{SbF}_3$
4. $\text{PhCH=CH}_2 + \text{PCl}_5 \longrightarrow \text{PhCH=CHPCl}_4 + \text{HCl}$
5. $\text{R}_2\text{P(S)P(S)R}_2 + \text{Cl}_2 \xrightarrow{h\nu} \text{RPhCl}_4$
6. $\text{CH}_3\text{PCl}_2 + \text{Cl}_2 \longrightarrow \text{CCl}_3\text{PCl}_4$
7. $\text{CClH}_2\text{PCl}_2 + \text{Cl}_2 \longrightarrow \text{CCl}_3\text{PCl}_4$
8. $(\text{RP})_4 + 4 \text{X}_2 \xrightarrow{4\text{X}_2} 4\text{RPX}_2 \xrightarrow{4\text{X}_2} 4\text{RPX}_4$
9. $3 \text{RPX}_2 + 4 \text{SbF}_3 \longrightarrow 3 \text{RPF}_4 + 2 \text{Sb} + 2 \text{SbX}_3$

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Vi phosphites, phosphates and their derivatives (PX_nY_{3-n} , $P(O)X_nY_{3-n}$; $X, Y=OH, OR$, halogens, NR_2)

分子式	構造式	化合物名	方法	収率	文献	物理定数
CH_3Cl_2OP	CH_3OPCl_2	Methyl dichlorophosphite	1	60	1, 12	(93/760)
CH_3ClFOP	CH_3OPClF	Methylchlorofluorophosphite	3	8	11	(38.9/760)
CH_3F_2OP	CH_3OPF_2	Methyldifluorophosphite	3	40	11, 12, 13	(-15.5/760)
$C_2H_4Cl_3OP$	$ClCH_2CH_2OPCl_2$	2-Chloroethyl dichlorophosphite	4, 5	72	14, 15	(77~81/40)
$C_2H_5Cl_2OP$	$C_2H_5OPCl_2$	Ethyl dichlorophosphite	1	52	2, 12	(25/25)
$C_3H_4BrF_3OP$	$CF_3(CH_2)CHOPBr_2$	1, 1, 1-Trifluoroisopropyl dibromophosphite	1	78	9	48, (156~157/760)
$C_3H_5Cl_2OP$	$CH_2=CHCH_2OPCl_2$	Allyl dichlorophosphite	1	50	7	(137/758)
$C_3H_7Cl_2OP$	$C_3H_7OPCl_2$	<i>n</i> -Propyl dichlorophosphite	1	—	3	(143~145/785)
$C_4H_9Cl_2OP$	$C_4H_9OPCl_2$	<i>n</i> -Butyl dichlorophosphite	1	50~70	4, 5, 6	(49~50/11)
$C_4H_9Br_2OP$	<i>i</i> -BuOPBr ₂	<i>iso</i> -Butyl dibromophosphite	1	—	8	(85~87/20)
$C_4H_7Cl_2O_2P$	$C_4H_5O_2CCH_2OPCl_2$	Carboethoxymethyl dichlorophosphite	1	62	6	(91~92/13)
$C_6H_5Cl_2OP$	$C_6H_5OPCl_2$	Phenyl dichlorophosphite	2	84	10	(90/10)
$C_6H_4Cl_3OP$	<i>p</i> -ClC ₆ H ₄ OPCl ₂	<i>p</i> -Chlorophenyl dichlorophosphite	2	85	10	(113~113.5/10) ^c
$C_4H_8Br_3O_2P$	$(BrCH_2CH_2O)_2PBr$	Bis(2-bromoethyl) bromophosphite	9	—	21	(115~119/2)
$C_6H_{10}ClO_2P$	$(C_2H_5O)_2PCl$	Diethyl chlorophosphite	6, 7	35.5	2, 23	(48~53/15)
$C_6H_{11}ClO_2P$	$(C_3H_7O)_2PCl$	Di- <i>n</i> -propyl chlorophosphite	6	54	16	(65~65.5/8)
$C_6H_{14}ClO_2P$	$(C_2H_5O_2CCH_2O)_2PCl$	Di-carboethoxymethyl chlorophosphite	6	55	17	(117/0.2)
$C_6H_{16}ClO_2P$	$(C_4H_9O)_2PCl$	Di- <i>n</i> -butyl chlorophosphite	6, 8	86	6, 22	(132~133/15)
$C_{12}H_{22}ClO_2P$	$(c-C_6H_{11}O)_2PCl$	Di-cyclohexyl chlorophosphite	6	45	17	(152~153/1)
$C_{12}H_{10}ClO_2P$	$(C_6H_5O)_2PCl$	Diphenyl chlorophosphite	10	62	24	(115/0.4)
$C_{14}H_{14}ClO_3P$	$(p-CH_3C_6H_4O)_2PCl$	Di- <i>p</i> -tolyl chlorophosphite	7	—	18, 20	(206~208/11)
$C_{14}H_{14}ClO_3P$	$(o-CH_3OC_6H_4O)_2PCl$	Di- <i>o</i> -anisyl chlorophosphite	7	—	19	—
$C_2H_7O_3P$	$(CH_3O)_2POH$	Dimethylphosphite	11	91	25, 26, 27	(37~43/6)
$C_4H_{11}O_3P$	$(C_2H_5O)_2POH$	Diethylphosphite	11	83~93	27	(73~74/14)
$C_6H_{15}O_3P$	$(C_3H_7O)_2POH$	Di- <i>n</i> -propylphosphite	11	93	27	—
$C_6H_{15}O_3P$	$(i-C_3H_7O)_2POH$	Di- <i>iso</i> -propylphosphite	11	87~90	26, 27, 28	(79/14)
$C_8H_{19}O_3P$	$(C_4H_9O)_2POH$	Di- <i>n</i> -butylphosphite	11	85~97	26, 27, 22	(126~127/18)
$C_{12}H_{23}O_3P$	$(c-C_6H_{11}O)_2POH$	Dicyclohexylphosphite	11	60~65	30a, 17	(120/0.15)
$C_6H_{11}O_3P$	$(CH_2=CHCH_2O)_2POH$	Diallylphosphite	11	42	31	(97~98/8)
$C_{14}H_{15}O_3P$	$(PhCH_2O)_2POH$	Dibenzylphosphite	12	57	32	(110~120/0.0005)
$C_{12}H_{11}O_3P$	$(PhO)_2POH$	Diphenylphosphite	12	97	33	(135~140/1~2)
$C_{16}H_{25}O_3P$	$(C_8H_{17}O)_2POH$	Diocetylphosphite	13	95	34	(190~191/3)
$C_3H_9O_3P$	$(CH_3O)_3P$	Trimethylphosphite	14	42.5	35	(110~111.5/745)
$C_6H_{15}O_3P$	$(C_2H_5O)_3P$	Triethylphosphite	14	87~92	35, 28, 36	(52/14)
$C_9H_{21}O_3P$	$(n-C_3H_7O)_3P$	Tri- <i>n</i> -propylphosphite	14	89	35	(82~84/10)
$C_{12}H_{27}O_3P$	$(n-BuO)_3P$	Tri- <i>n</i> -butylphosphite	14	91~96	35, 22	(122~123/12)
$C_9H_{15}O_3P$	$(CH_2=GHCH_2O)_3P$	Triallylphosphite	14	75	37, 38	(55~60/0.5)
$C_{21}H_{21}O_3P$	$(PhCH_2O)_3P$	Tribenzylphosphite	14	91	39, 40	65(140/1)
$C_4H_{11}O_3P$	$(CH_3O)_2(OC_2H_5)P$	Dimethylethylphosphite	16	—	41	(28~29/14)
$C_{18}H_{21}O_3P$	$(PhO)_2(c-C_6H_{11}O)P$	Diphenylcyclohexylphosphite	16	88	42	(148~153/0.3)
$C_{15}H_{17}O_3P$	$(PhO)_2(PrO)P$	Diphenylpropylphosphite	16	59	43	(203~204/24)
$C_{18}H_{33}O_3P$	$(c-C_6H_{11}O)_3P$	Tricyclohexylphosphite	14	66.5	44	(142~144/1)

分子式	構造式	化合物名	方法	収率	文献	物理定数
C ₁₈ H ₁₅ O ₃ P	(PhO) ₃ P	Triphenylphosphite	15	94	45	21~23, (183~184/1)
C ₂₁ H ₂₁ O ₃ P	(<i>p</i> -CH ₃ C ₆ H ₄ O) ₃ P	Tri- <i>p</i> -tolylphosphite	15	85.7	46, 18	(194/1)
C ₃₀ H ₂₁ O ₃ P	(<i>β</i> -C ₁₀ H ₇ O) ₃ P	Tri- <i>β</i> -naphthylphosphite	15	70	47	94
C ₂ H ₅ Cl ₂ NP	(CH ₃) ₂ NPCl ₂	(Dimethylamino) dichlorophosphine*	17	58	48, 49, 52	(40/10)
C ₂ H ₅ F ₂ NP	(CH ₃) ₂ NPF ₂	(Dimethylamino) difluorophosphine	18	65	53, 54	(56/60)
C ₄ H ₁₀ Cl ₂ NP	(C ₂ H ₅) ₂ NPCl ₂	(Diethylamino) dichlorophosphine	17	70	50	(72/11)
C ₄ H ₁₀ F ₂ NP	(C ₂ H ₅) ₂ NPF ₂	(Diethylamino) difluorophosphine	18	57	54	(28/32)
C ₈ H ₁₈ Cl ₂ NP	(C ₄ H ₉) ₂ NPCl ₂	(Di- <i>n</i> -butylamino) dichlorophosphine	17	75	51	37~38, (116~117/10)
C ₄ H ₁₂ ClN ₂ P	[(CH ₃) ₂ N] ₂ PCl	Bis(dimethylamino) chlorophosphine	19	91.5	55	(29/1)
C ₆ H ₁₈ N ₃ P	[(CH ₃) ₂ N] ₃ P	Tris(dimethylamino) phosphine	20	46	49	(52/14)
C ₁₂ H ₂₄ O ₃ N ₃ P	(OC ₄ H ₉ N) ₃ P	Phosphorus trimorphoride	20	80.5	59	154
C ₁₂ H ₃₀ N ₃ P	[(C ₂ H ₅) ₂ N] ₃ P	Tris(diethylamino) phosphine	20	66.8	56	(120~122/10)
C ₁₅ H ₃₀ N ₃ P	(C ₃ H ₁₀ N) ₃ P	Phosphorus tripiperidide Phosphine	20	65	58	37~38
C ₁₈ H ₄₂ N ₃ P	[(C ₃ H ₇) ₂ N] ₃ P	Tris(di- <i>n</i> -propylamino) phosphine	20	90	56	(101~103/0.15)
C ₂₄ H ₅₄ N ₃ P	[(C ₄ H ₉) ₂ N] ₃ P	Tris(di- <i>n</i> -butylamino) phosphine	20	67	56	(140~142/0.1)
C ₄₂ H ₄₈ N ₃ P	[Ph(Me)N] ₃ P	Phosphorus tri(<i>N</i> -metylanilide)	20	86	57	208~209
CH ₃ O ₃ P	CH ₃ OP(O)(OH) ₂	Methyl dihydrogen phosphate	21	90	61	195~198(dec)
C ₂ H ₅ O ₄ P	C ₂ H ₅ OP(O)(OH) ₂	Ethyl dihydrogen phosphate (Ba salt)	21	89	62	—
C ₄ H ₁₁ O ₄ P	C ₄ H ₉ OP(O)(OH) ₂	<i>n</i> -Butyl dihydrogen phosphate (Ba salt)	21	56	63	—
C ₆ H ₅ ClO ₃ P	<i>p</i> -ClC ₆ H ₄ OP(O)(OH) ₂	<i>p</i> -Chlorophenyl dihydrogen phosphate	22	—	68, 69	93
C ₆ H ₁₃ O ₃ P	<i>c</i> -C ₆ H ₁₁ OP(O)(OH) ₂	Cyclohexyl dihydrogen phosphate (Ba salt)	21	85	61	—
C ₆ H ₇ O ₃ P	PhOP(O)(OH) ₂	Phenyl dihydrogen phosphate	21, 22	68	64, 66	97~98
C ₇ H ₉ O ₃ P	<i>p</i> -CH ₃ C ₆ H ₄ OP(O)(OH) ₂	<i>p</i> -Tolyl dihydrogen phosphate	22	—	67	116
C ₇ H ₉ O ₃ P	PhCH ₂ OP(O)(OH) ₂	Benzyl dihydrogen phosphatate	21	94	61	94~96
C ₁₀ H ₉ O ₃ P	<i>β</i> -C ₁₀ H ₇ OP(O)(OH) ₂	<i>β</i> -Naphthyl dihydrogen phosphate	21	80	65	172~173
CH ₃ Cl ₂ O ₂ P	CH ₃ OP(O)Cl ₂	Methyl phosphorodichloride*	23	—	70, 71	(62~64/15)
C ₂ H ₅ Cl ₂ O ₂ P	C ₂ H ₅ OP(O)Cl ₂	Ethyl phosphorodichloride	23	87	70, 72, 73	(34/2)
C ₃ H ₇ Cl ₂ O ₂ P	C ₃ H ₇ OP(O)Cl ₂	<i>n</i> -Propyl phosphorodichloride	23	77	70	(69~72/13)
C ₄ H ₉ Cl ₂ O ₂ P	C ₄ H ₉ OP(O)Cl ₂	<i>n</i> -Butyl phosphorodichloride	23	85	70, 73, 22	(80~82/10)
C ₆ H ₅ Cl ₂ O ₂ P	C ₆ H ₅ OP(O)Cl ₂	Phenyl phosphorodichloride	24	95.8	74, 75	(106~107.5/7)
C ₇ H ₇ Cl ₂ O ₂ P	<i>p</i> -CH ₃ C ₆ H ₄ OP(O)Cl ₂	<i>p</i> -Tolyl phosphorodichloride	24	85.5	75	(90~91/1)
C ₆ H ₄ Cl ₂ O ₂ P	<i>p</i> -ClC ₆ H ₄ OP(O)Cl ₂	<i>p</i> -Chlorophenyl phosphorodichloride	24	75.4	75	(96~104/1~1.5)
C ₆ H ₄ Cl ₂ NO ₄ P	<i>p</i> -O ₂ N-C ₆ H ₄ OP(O)Cl ₂	<i>p</i> -Nitrophenyl phosphorodichloride	24	88.1	74	(144/1)
C ₂ H ₅ ClFO ₂ P	C ₂ H ₅ OP(O)ClF	Ethyl phosphorochloridofluoride	25	69.2	76	(50/0.5)
C ₂ H ₅ BrFO ₂ P	C ₂ H ₅ OP(O)BrF	Ethyl phosphorobromidofluoride	25	21	76	(40~42/0.15)
C ₆ H ₅ ClFO ₂ P	C ₆ H ₅ OP(O)ClF	Phenyl phosphorochloridofluoride	25	87	77	(66~70/5)
C ₂ H ₅ F ₂ O ₂ P	C ₂ H ₅ OP(O)F ₂	Ethyl phosphorodifluoride	26	42	78	(86~88/760)
C ₂ H ₅ Cl ₂ NOP	(CH ₃) ₂ NP(O)Cl ₂	Dimethylphosphoramidic dichloride	27	88~95	79	(90~91/22)
C ₆ H ₁₅ O ₄ P	(C ₂ H ₅ O) ₃ PO	Triethyl phosphate	28	51.7	80	(104~107/16)
C ₉ H ₂ O ₄ P	(C ₃ H ₇ O) ₃ PO	Tri- <i>n</i> -propyl phosphate	28	63.5	80, 91	(128~134/15)

分 子 式	構 造 式	化 合 物 名	方法	収 率	文 献	物 理 定 数
$C_9H_{21}O_4P$	$(iso-C_3H_7O)_3PO$	Tri- <i>i</i> -propyl phosphate	27	95	81	(140/10)
$C_{12}H_{27}O_4P$	$(C_4H_9O)_3PO$	Tri- <i>n</i> -butyl phosphate	28	98	80, 81 82, 22	(153~154/9)
$C_{12}H_{27}O_4P$	$(sec-C_4H_9O)_3PO$	Tri- <i>sec</i> -butyl phosphate	28	40~45	90	—
$C_{15}H_{33}O_4P$	$(C_5H_{11}O)_3PO$	Tri- <i>n</i> -amyl phosphate	28	60~65	91	—
$C_{18}H_{33}O_4P$	$(c-C_6H_{11})_3PO$	Tricyclohexyl phosphate	28	90	81	59
$C_9H_{15}O_4P$	$(CH_2=CH-CH_2-O)_3PO$	Triallyl phosphate	28	74	83, 84	(80~90/1.5)
$C_{18}H_{12}Cl_3O_4P$	$(o-Cl-C_6H_4O)_3PO$	Tri- <i>o</i> -chlorophenyl phosphate	29	—	90	37
$C_{18}H_{15}O_4P$	$(PhO)_3PO$	Triphenyl phosphate	29	81~95	85, 86, 87	45
$C_{21}H_{21}O_4P$	$(p-CH_3C_6H_4O)_3PO$	Tri- <i>p</i> -tolyl phosphate	29	80~97	86, 87	77.5~78
$C_{21}H_{21}O_4P$	$(m-CH_3C_6H_4O)_3PO$	Tri- <i>m</i> -tolyl phosphate	29	71	88	(151~154/0.15)
$C_{36}H_{27}O_4P$	$(PhC_6H_4O)_3PO$	Tri-4-biphenyl phosphate	29	—	89	114
$C_{30}H_{21}O_4P$	$(\alpha-C_{10}H_7O)_3PO$	Tri- α -naphthyl phosphate	29	60	87	144.5~145
$C_4H_{12}NO_3P$	$(C_2H_5O)_2P(O)NH_2$	Diethyl phoramidate	30	90	92	46~47
H_6N_3OP	$(H_2N)_3PO$	Phosphoric triamide	31	70	93	—
$C_2H_6ClO_3P$	$(CH_3O)_2P(O)Cl$	Dimethyl phosphorochloridate	32	83	94, 96, 97	(55~57/2~3)
$C_4H_{10}ClO_3P$	$(C_2H_5O)_2P(O)Cl$	Diethyl phosphorochloridate	32	90	27, 95, 98	(93~95/18)
$C_6H_{14}ClO_3P$	$(C_3H_7O)_2P(O)Cl$	Di- <i>n</i> -propyl phosphorochloridate	32	92	95, 96	(76/1.5)
$C_8H_{14}ClO_3P$	$(i-C_3H_7O)_2P(O)Cl$	Diisopropyl phosphorochloridate	32	82~90	28, 99, 100	(68/2)
$C_8H_{18}ClO_3P$	$(C_4H_9O)_2P(O)Cl$	Di- <i>n</i> -butyl phosphorochloridate	32	90	94, 27, 95	(132~133/18)
$C_{12}H_{10}ClO_3P$	$(PhO)_2P(O)Cl$	Diphenyl phosphorochloridate	33	—	85, 101	(191~94/12)
$C_{24}H_{18}ClO_3P$	$(PhC_6H_4O)_2P(O)Cl$	Di-4-biphenyl phosphorochloride	33	60	102	148~158(270/0.01)
$C_4H_{12}ClN_2OP$	$(Me_2N)_2P(O)Cl$	Tetramethylphosphorodiamidic chloride	34	95	103	(63/1)
$C_4H_{11}O_4P$	$(C_2H_5O)_2P(O)OH$	Diethyl phosphate	35	90	104	—
$C_6H_{15}O_4P$	$(C_3H_7O)_2P(O)OH$	Di- <i>n</i> -propyl phosphate	35	25	105	—
$C_{14}H_{15}O_4P$	$(PhCH_2O)_2P(O)OH$	Dibenzyl phosphate	35	96	104, 106, 107	79
$C_{12}H_{11}O_4P$	$(PhO)_2P(O)OH$	Diphenyl phosphate	35, 36	98	107	70
$C_{16}H_{15}O_4P$	$C_3H_7O(PhCH_2O)P(O)OH$	<i>n</i> -Propylbenzylphosphate	35	50	107	293~297(Ca salt)
$C_{16}H_{15}O_4P$	$i-C_3H_7O(PhCH_2O)P(O)OH$	<i>i</i> -Propylbenzylphosphate	35	63	107	268~272
$C_8H_{19}O_4P$	$(C_4H_9O)_2P(O)OH$	Di- <i>n</i> -butyl phosphate	37	79	110	—
$C_{12}H_9Cl_2O_4P$	$(ClC_6H_4O)_2P(O)OH$	Bis(chlorophenyl) phosphate	36	76	108	133~135
$C_{24}H_{19}O_4P$	$(PhC_6H_4O)_2P(O)OH$	Dibiphenyl phosphate	36	75	102	232~234
$C_{26}H_{15}O_4P$	$(\alpha-C_{10}H_7O)_2P(O)OH$	Di- α -naphthylphosphate	36	94	109	137~139

方 法

- $PX_3 + ROH \xrightarrow{\text{Amine}} ROPX_2$
- $PX_3 + ArOH \xrightarrow{\text{Amine}} ArOPX_2$
- $ROPX_2 + SbF_3 \longrightarrow ROPF_2 \text{ or } ROPClF$
- $\text{CH}_2-\text{CH}_2 + PCl_3 \longrightarrow \text{ClCH}_2\text{CH}_2\text{OPCl}_2$
- $\text{ClCH}_2\text{CH}_2\text{OH} + PCl_3 \longrightarrow \text{ClCH}_2\text{CH}_2\text{OPCl}_2$
- $2ROH + PCl_3 \xrightarrow{\text{Amine}} (RO)_2PCl$

- $2ArOH + PCl_3 \longrightarrow (ArO)_2PCl$
- $2(RO)_3P + PCl_3 \longrightarrow 3(RO)_2PCl$
- $2\text{CH}_2-\text{CH}_2 + PBr_3 \longrightarrow (\text{BrCH}_2\text{CH}_2\text{O})_2PBr$
- $(RO)_3P + \text{CH}_3\text{CH}_2\text{COCl} \longrightarrow (RO)_2PCl + \text{CH}_3\text{CH}_2\text{CO}_2\text{Et}$
- $ROH + PX_3 \longrightarrow (RO)_2P(O)H + RX$
- $(RO)_2PCl + H_2O \longrightarrow (RO)_2P(O)H$
- $(EtO)_2P(O)H + 2C_8H_{17}OH \longrightarrow (C_8H_{17}O)_2P(O)H$

14. $\text{PCl}_3 + 3\text{ROH} \xrightarrow{\text{Amine}} (\text{RO})_3\text{P}$
 15. $\text{PCl}_3 + 3\text{ArOH} \longrightarrow (\text{ArO})_3\text{P}$
 16. $(\text{RO})_2\text{PX} + \text{R}'\text{OH} \longrightarrow (\text{RO})_2\text{POR}'$
 17. $\text{PCl} + 2\text{R}_2\text{NH} \longrightarrow \text{R}_2\text{NPCl}_2 + \text{R}_2\text{NH} \cdot \text{HCl}$
 18. $\text{R}_2\text{NPCl}_2 + 2\text{MF} \longrightarrow \text{R}_2\text{NPF}_2 + 2\text{MCl}$
 19. $2(\text{R}_2\text{N})_3\text{P} + \text{PCl}_3 \longrightarrow 3(\text{R}_2\text{N})_2\text{PCl}$
 20. $6\text{R}_2\text{NH} + \text{PCl}_3 \longrightarrow (\text{R}_2\text{N})_3\text{P} + 3\text{R}_2\text{NH} \cdot \text{HCl}$
 21. $(\text{R}'\text{O})_2\text{P}(\text{O})\text{OR} + \text{H}_2\text{O} \xrightarrow{\text{Catalyst}} \text{ROP}(\text{O})(\text{OH})_2$
 22. $\text{ROP}(\text{O})\text{X}_2 + \text{H}_2\text{O} \longrightarrow \text{ROP}(\text{O})(\text{OH})_2$
 23. $\text{ROH} + \text{POX}_3 \longrightarrow \text{ROP}(\text{O})\text{X}_2 + \text{HX}$
 24. $\text{ArOH} + \text{POX}_3 \xrightarrow{\text{Catalyst}} \text{ArOP}(\text{O})\text{X}_2 + \text{HX}$
 25. $\text{P}(\text{O})\text{X}_2\text{Y} + \text{ROH} \longrightarrow \text{ROP}(\text{O})\text{X}_2 + \text{HY}$
 26. $\text{ROP}(\text{O})\text{Cl}_2 + 2\text{NaF} \longrightarrow \text{ROP}(\text{O})\text{F}_2 + 2\text{NaCl}$
 27. $\text{Me}_2\text{NP}(\text{O})\text{Cl}_2 + 2\text{Me}_2\text{NH} \longrightarrow (\text{Me}_2\text{N})_2\text{P}(\text{O})\text{Cl} + \text{Me}_2\text{NH} \cdot \text{HCl}$
 28. $\text{POCl}_3 + 3\text{ROH} \xrightarrow{\text{Amine}} (\text{RO})_3\text{PO}$
 29. $\text{POCl}_3 + 3\text{ArOH} \xrightarrow{\text{AlCl}_3, \text{MgCl}_2} (\text{ArO})_3\text{PO}$
 30. $(\text{EtO})_2\text{POH} + \text{CCl}_4 + 2\text{NH}_3 \longrightarrow (\text{EtO})_2\text{P}(\text{O})\text{NH}_2 + \text{CHCl}_3 + \text{NH}_4\text{Cl}$
 31. $\text{POCl}_3 + 6\text{NH}_3 \longrightarrow (\text{NH}_2)_3\text{PO} + 3\text{NH}_4\text{Cl}$
 32. $(\text{RO})_2\text{POH} + \text{SOCl}_2 \text{ or } \text{Cl}_2 \longrightarrow (\text{RO})_2\text{P}(\text{O})\text{X} + \text{HX}$
 33. $\text{POX}_3 + 2\text{ArOH} \longrightarrow (\text{ArO})_2\text{P}(\text{O})\text{X} + 2\text{HX}$
 34. $\text{Me}_2\text{NP}(\text{O})\text{Cl}_2 + 2\text{Me}_2\text{NH} \longrightarrow (\text{Me}_2\text{N})_2\text{P}(\text{O})\text{Cl} + \text{Me}_2\text{NH} \cdot \text{HCl}$
 35. $(\text{RO})_3\text{POXY} \longrightarrow (\text{RO})_2\text{P}(\text{O})\text{OH}$
 36. $(\text{ArO})_2\text{P}(\text{O})\text{X} + \text{H}_2\text{O} \longrightarrow (\text{ArO})_2\text{P}(\text{O})\text{OH}$
 37. $(\text{RO})_2\text{P}(\text{O})\text{H} + \text{SO}_2\text{Cl}_2 \text{ or } \text{Cl}_2 \xrightarrow{\text{H}_2\text{O}} (\text{RO})_2\text{P}(\text{O})\text{Cl} \xrightarrow{\text{H}_2\text{O}} (\text{RO})_2\text{P}(\text{O})\text{OH}$
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