Synthesis of Some Novel Carboxylic Acids and Insecticidal Activity of Their Esters[†]

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Various novel acyclic carboxylic acids were prepared and some of their 3-phenoxybenzyl esters were found to have slight insecticidal activity.

One of the useful acid moieties of a number of synthetic pyrethroids¹⁾ is α -isopropyl-4-chlorophenylacetic acid.²⁾ This paper reports the synthesis of some new carboxylic acids in which the phenyl or the isopropyl group of α -isopropylphenylacetic acid is replaced with other groups, and the insecticidal activity of their 3-phenoxybenzyl esters.

Methyl 3-pentenoate³⁾ and ethyl 3-hexenoate³⁾ were alkylated at α -position with ethyl or isopropyl halides, and the alkylated products were hydrolyzed to acids (1, 2, 3) (Fig. 1). The acids were analyzed by PMR.

Alkylation of ethyl crotonate with isopropyl iodide in the presence of LDA gave the ester 4, but hydrolysis of 4 gave a mixture of acids 5 and 6 (2:3). Alkylation of *tert*-butyl crotonate in the presence of sodium amide gave a mixture of 7 and 8 (2:1), and when 0.8 mol eq. of the base was used the ratio of 7 and 8 was 3:1 (Fig. 1).

The nitrile 13, prepared by alkylation of 12, was hydrolyzed to the carboxylic acid 14. The bromide 11 was prepared from the ester 9 *via* the alcohol 10 and alternatively bromination of dimethylbutene by NBS gave the same bromide.

This bromide 11 was converted to the nitrile

FIG. 1.

12 by the usual method (Fig. 2).

The above acids (1, 2, 3, 5, 6, 14) were converted to acid chlorides and esterified with 3-phenoxybenzyl alcohol (Fig. 3).

The esters 16 and 17 were converted to the corresponding dichlorocyclopropane derivatives 20 and 21 or oxidized to the corresponding epoxides 22 and 23 respectively (Fig. 4).

Table I shows the insecticidal activities of nine 3-phenoxybenzyl carboxylates on mosquitoes and houseflies.

Compounds 16 and 17 were active on both insects and the esters 18 (a mixture of 5 and 6) showed a low activity on mosquitoes.

[†] Studies on Chrysanthemic Acid. Part XXIX. For Part XXVIII, see ref. 4.

FIG. 2.

15	RCOOH = 1
16	= 2
17	= 3
18	= 5 + 6
19	= 14

FIG. 3.

FIG. 4.

EXPERIMENTAL

All boiling points were uncorrected. IR spectra were referred to films on a JASCO IRA-1 spectrometer. PMR spectra were recorded on a JEOL (JNM-MH 100) spectrometer or on a Hitachi R-24A spectrometer with TMS as an internal standard.

Methyl 2-ethyl-3-pentenoate. Methyl 3-pentenoate³⁾ (4.4 g) was added to a solution of sodium amide prepared from sodium metal (0.9 g) in liq ammonia over 30 min and the solution was stirred for additional 30 min.

Ethyl bromide (8.8 ml) was added dropwise to the above solution and after the solution was stirred for 1 hr, ammonium chloride (1.72 g) was added. The solution was left to stand overnight at room temperature and ice-cooled 5% HCl solution was added. The solution was extracted with ether and the extract was washed with sat NaHCO₃

TABLE I. TOXICITIES OF 3-PHENOXYBENZYL CARBOXYLATES TO MOSQUITOES AND HOUSEFLIES

Compounds	Mortality			
	Mosquitoes		Houseflies	
	0.5 ppm	5 ppm	50 ppm	500 ppm
15	0	0	0	0
16	13.3	95.0	0	100
17	10.0	61.7	0	100
18	0	86.7	0	0
19	0	0	0	0
20	0	1.7	0	0
21	0	0	0	0
22	0	0	0	0
23	0	0	0	0
Phenothrin* (LC ₅₀)	0.06 ppm		18.0 ppm	

* 3-Phenoxybenzyl (±)-*cis,trans*-chrysanthemate.

solution, brine and dried over MgSO₄. The solution was concentrated and the residue was distilled to give 3.4 g (60%) of methyl 2-ethyl-3-pentenoate, bp 89~92°C (45 mmHg); n_D^{24} 1.4266; IR $\nu_{\max}$ cm⁻¹: 1745, 1360; PMR (60 MHz, CDCl₃) δ : 0.9 (3H, t, J =7 Hz, C-CH₃), 1.1~1.6 (2H, m, CH₂), 1.7 (3H, d, J =3 Hz, CH₃-C=C), 2.9 (1H, m, CH), 3.7 (3H, s, CO₂CH₃), 5.4~5.7 (2H, m, CH=CH).

Methyl 2-isopropyl-3-pentenoate. Methyl 3-pentenoate (7.47 g) was alkylated with isopropyl iodide (12.25 g) in a manner similar to that described for the preparation of methyl 2-ethyl-3-pentenoate to give 6.95 g (68%) of methyl 2-isopropyl-3-pentenoate, bp 80~85°C (50 mmHg); n_D^{25} 1.4275; IR $\nu_{\max}$ cm⁻¹: 1745, 1440; PMR (60 MHz, CCl₄) δ : 0.85 and 0.96 (each 3H, d, J =6 Hz, (CH₃)₂), 1.7 (3H, d, J =4 Hz, C=C-CH₃), 1.9~2.3 (1H, m, CHMe₂), 2.7 (1H, d-d, J =7 Hz, CH-CO₂Me), 3.7 (3H, s, CO₂CH₃), 5.4~5.7 (2H, m, CH=CH).

2-Ethyl-3-pentenoic acid (1). Methyl 2-ethyl-3-pentenoate (1.6 g) was dissolved in methanol (4 g) containing sodium hydroxide (0.43 g) and the solution was left to stand overnight at room temperature. The solution was poured into water and the solution was washed with ether. The aqueous solution was acidified with 5% HCl solution and extracted with ether. The extract was dried over Na_2SO_4 and concentrated to give 0.80 g (56%) of **1**; PMR (60 MHz, CDCl_3) δ : 0.9 (3H, t, $J=7$ Hz, $\text{C}-\text{CH}_3$), 1.1~1.6 (2H, m, CH_2), 1.7 (3H, d, $J=4$ Hz, $\text{CH}_3-\text{C}=\text{C}$), 2.9 (1H, m, CH), 5.4~5.7 (2H, m, $\text{CH}=\text{CH}$), 10.5 (1H, bs, COOH).

2-Isopropyl-3-pentenoic acid (2). Methyl 2-isopropyl-3-pentenoate was treated as described for the acid **1** to give 1.78 g (56%) of **2**; PMR (60 MHz, CCl_4) δ : 0.85 and 0.96 (each 3H, d, $J=6$ Hz, $(\text{CH}_3)_2$), 1.7 (3H, d, $J=4$ Hz, $\text{CH}_3-\text{C}=\text{C}$), 1.9~2.4 (1H, m, CHMe_2), 2.7 (1H, d-d, $J=7$ Hz and 1 Hz, $\text{CH}-\text{CO}_2$), 5.4~5.7 (2H, m, $\text{CH}=\text{CH}$), 10.5 (1H, bs, COOH).

Ethyl 2-isopropyl-3-hexenoate. Ethyl 3-hexenoate³⁾ (29.9 g) and isopropyl iodide (42.8 g) were treated as described for methyl 2-ethyl-3-pentenoate.

Distillation of the crude product gave 29.7 g (77%) of ethyl 2-isopropyl-3-pentenoate, bp 110~117°C (48 mmHg); PMR (60 MHz, CCl_4) δ : 0.8~1.1 (9H, m, $\text{CH}_3 \times 3$), 1.23 (3H, t, $J=7$ Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$), 1.8~2.3 (3H, m, $\text{CH}_2-\text{C}=\text{C}$ and CHMe_2), 2.55 (1H, d-d, $J=8$ Hz and 1 Hz, $\text{CH}-\text{CO}_2\text{Et}$), 4.15 (2H, q, $J=7$ Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$), 3.4~3.65 (2H, m, $\text{CH}=\text{CH}$).

2-Isopropyl-3-hexenoic acid (3). Ethyl 2-isopropyl-3-hexenoate (29.7 g) was treated as described for the acid **1** to give 18.4 g (72%) of **3**, PMR (60 MHz, CCl_4) δ : 0.8~1.3 (9H, m, $\text{CH}_3 \times 3$), 1.8~2.3 (3H, m, $\text{CH}_2-\text{C}=\text{C}$ and CHMe_2), 2.6 (1H, d-d, $J=8$ Hz and 1 Hz), 5.4~5.7 (2H, m, $\text{CH}=\text{CH}$), 11.9 (1H, s, COOH).

Ethyl 2-isopropyl-3-butenate (4). HMPA (8.7 g) was added to lithium diisopropylamide in THF (40 ml) prepared from diisopropylamine (9 g) and *n*-butyllithium (33.7 ml, 1.43 M) at -70°C . After 30 min ethyl crotonate (5 g) in THF (20 ml) was added to the solution under stirring. After 10 min isopropyl iodide (8.95 g) in THF (20 ml) was added to the above solution and the solution was stirred for 3 hr at -70°C .

Ammonium chloride (10 g) was added and the solution was poured into ice-water. The solution was extracted with ether three times and the extract was washed by 2.5% HCl aq. solution, water and dried over MgSO_4 . The solution was concentrated and the residue was distilled to give 3.60 g of **4** (53%), bp 75~85°C (50 mmHg); PMR (60 MHz, CDCl_3) δ : 0.85 and 0.96 (each 3H, d, $J=6$ Hz, $(\text{CH}_3)_2$), 1.25 (3H, t, $J=8$ Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$), 1.8~2.3 (1H, m, CHMe_2), 2.7 (1H, d-d, $J=8$ Hz and 1 Hz, CHCO_2Et), 4.2 (2H, q, $J=8$ Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$), 4.95~5.3

(2H, m, $\text{CH}_2=\text{C}$), 5.60~6.1 (1H, m, $\text{C}=\text{CH}$).

Hydrolysis of ethyl 2-isopropyl-3-butenate (4). The ester **4** (3.60 g) was hydrolyzed with methanolic NaOH. Based on PMR analysis the product was found to be a mixture (1.80 g) of 2-isopropyl-3-butenic acid (**5**) and 2-isopropyl-2-butenic acid (**6**) in the ratio of 2:3. PMR (60 MHz, CDCl_3) δ : 0.90 and 1.05 (each 3H, d, $J=4$ Hz, $\text{C}-\text{C}(\text{CH}_3)_2$), 1.2 (6H, d, $J=7$ Hz, $\text{C}=\text{C}-\text{C}(\text{CH}_3)_2$), 1.7~2.4 (1H, m, CHMe_2), 1.85 (3H, d, $J=7$ Hz, $\text{CH}_3-\text{C}=\text{C}$), 2.6~3.2 (1H, d-d, $J=8$ Hz and 1 Hz, $\text{C}=\text{C}-\text{CHCO}_2\text{H}$), 5.0~5.35 (2H, m, $\text{CH}_2=\text{C}$), 5.60~6.1 (1H, m, $\text{CH}_2=\text{CH}$), 6.95 (1H, q, $J=7$ Hz, $\text{CH}_3\text{CH}=\text{C}$), 10.4 (1H, bs, COOH).

Alkylation of tert-butyl crotonate. *tert*-Butyl crotonate (5 g) was alkylated with isopropyl iodide in the presence of NaNH_2 , and the crude product was distilled. Based on PMR analysis the distillate was found to be a mixture (1.42 g, 22%) of *tert*-butyl 2-isopropyl-3-butenate (**7**) and *tert*-butyl 2-isopropyl-2-butenate (**8**) in the ratio of 2:1. bp 85~95°C (50 mmHg); n_D^{25} 1.4291; IR ν_{max} cm^{-1} : 1740, 1720, 1650; PMR (60 MHz, CDCl_3) δ : 0.85 and 0.95 (each 3H, d, $J=4$ Hz, $\text{CC}(\text{CH}_3)_2$), 1.15 (6H, d, $J=7$ Hz, $\text{C}=\text{CC}(\text{CH}_3)_2$), 1.45 (9H, s, $(\text{CH}_3)_3$), 1.47 (9H, s, $(\text{CH}_3)_3$), 1.75 (3H, d, $J=7$ Hz, $\text{CH}_3\text{C}=\text{C}$), 1.7~2.1 (1H, m, CHMe_2), 2.6 (1H, d-d, $J=8$ Hz and 1 Hz, $\text{C}=\text{CCHCO}_2t\text{-Bu}$), 4.9~5.3 (2H, m, $\text{CH}_2=\text{C}$), 5.55~6.1 (1H, m, $\text{CH}=\text{CH}_2$), 6.55 (1H, q, $J=7$ Hz, $\text{CH}_3\text{CH}=\text{C}$).

Ethyl 2,3-dimethyl-2-butenate (9). Ethyl α -(diethoxyphosphinyl)propionate (243.3 g) was added dropwise to a suspension of sodium hydride (50.5 g as 50% oil dispersion) in dry benzene (500 ml) at room temperature, and then the solution was stirred for 30 min.

Acetone (47 g) in benzene (300 ml) was added dropwise to the above ice-cooled solution and the solution was stirred for 1 hr at room temperature. The bath temperature was raised slowly to 50°C in 1 hr and the solution was stirred for an additional 1 hr at 50°C . After standing overnight at room temperature the solution was poured into water and extracted with ether. The extract was washed with water three times, dried over MgSO_4 and concentrated. The residue was distilled to give 64.2 g of **9** (56%), bp 74~75°C (45 mmHg); n_D^{25} 1.4416; IR ν_{max} cm^{-1} : 1720, 1640; PMR (60 MHz, CCl_4) δ : 1.3 (3H, t, $J=7$ Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$), 1.85 (6H, s, $(\text{CH}_3)_2\text{C}=\text{C}$), 2.0 (3H, s, $\text{C}=\text{C}(\text{CH}_3)\text{CO}_2\text{Et}$), 4.15 (2H, q, $J=7$ Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$).

2,3-Dimethyl-2-butene-1-ol (10). The ester **9** (61.5 g) in ether (330 ml) was added dropwise to an ice-cooled solution of lithium aluminum hydride (13.1 g) in ether (330 ml) under stirring. The mixture was left to stand overnight at room temperature and then heated under reflux for 2 hr. After cooling, water (13 ml), 15% NaOH aq (13 ml), and water (40 ml) were added to the stirred and ice-cooled mixture.

After stirring for 1 hr THF (300 ml) was added and the mixture was stirred for 30 min. Then it was filtered and the filter cake was washed with THF three times. The combined organic solution was dried over Na_2SO_4 and concentrated. The residue was distilled to give 40.2 g of **10** (92%), n_D^{22} 1.4549; IR ν_{max} cm^{-1} : 3600~3100, 1660, 1005; PMR (100 MHz, CDCl_3): 1.65 (3H, s, CH_3), 1.70 (6H, s, $\text{CH}_3 \times 2$), 4.1 (2H, s, CH_2).

1-Bromo-2,3-dimethyl-2-butene (11).

From allyl alcohol **10**. Phosphorus tribromide (2 g) in dry ether (7 ml) was added dropwise to alcohol (**10**, 2 g) in dry ether (10 ml) at -10°C under stirring. After 4 hours the mixture was poured into ice-water and was extracted with ether. The extract was washed with water, saturated sodium bicarbonate solution, water and dried over MgSO_4 . The solution was concentrated *in vacuo* to give 1.3 g (40%) of **11**. IR ν_{max} cm^{-1} : 1660, 1460; PMR (100 MHz, CCl_4) δ : 1.75 (3H, s, CH_3), 1.80 (6H, s, $\text{CH}_3 \times 2$), 4.0 (2H, s, CH_2).

From 2,3-dimethyl-2-butene. The mixture of 2,3-dimethyl-2-butene (100 g), *N*-bromosuccinimide (211.5 g), benzoylperoxide (1 g) and CCl_4 (250 g) was stirred at 70°C overnight. The mixture was filtered and the filtrate was concentrated and distilled to give 10.6 g of **11** (36.5%), bp $60\sim 62.5^\circ\text{C}$ (36 mmHg). This bromide was purified by fractional distillation. bp $53.5\sim 53.9^\circ\text{C}$ (28 mmHg), n_D^{22} 1.4946.

This bromide was spectroscopically (IR and PMR) identical with that prepared from allyl alcohol **10**.

3,4-Dimethyl-3-pentenitrile (12). Sodium cyanide (31.6 g) was added to the bromide **11** (6 g) in DMSO (40 ml) and the mixture was stirred for 30 min at 50°C . The mixture was left to stand overnight at room temperature and poured into ice-water. The solution was extracted with methylene chloride and the extract was washed with water and dried over MgSO_4 . The extract was concentrated and distilled to give 1.74 g (43.3%) of **12**, bp $77\sim 80^\circ\text{C}$ (33 mmHg); n_D^{22} 1.4489; IR ν_{max} cm^{-1} : 2240, 1440, 1420; PMR (100 MHz, CCl_4) δ : 1.70 (6H, s, $\text{CH}_3 \times 2$), 1.80 (3H, s, CH_3), 3.0 (2H, s, CH_2).

2-Isopropyl-3,4-dimethyl-3-pentenitrile (13). The nitrile **12** (1.0 g) in 4 ml dry benzene was added to lithium hexamethyldisilyl amide in benzene (30 ml) (prepared from hexamethyldisilazane (1.77 g) and *n*-BuLi (6 ml, 1.84 M) at 10°C) and the mixture was stirred at 10°C for 2 hr. Isopropyl bromide (2.25 g) in benzene (10 ml) was added to the above ice-cooled solution and the mixture was stirred at room temperature overnight. The solution was washed with water, 2% HCl aq soln, water and dried over MgSO_4 . Evaporation of the solvent gave 1.23 g (89%) of **18**, n_D^{22} 1.4535; IR ν_{max} cm^{-1} : 2230, 1460; PMR (100 MHz, CCl_4) δ : 0.85 and 1.2 (each 3H, d, $J=6$ Hz, $\text{C}(\text{CH}_3)_2$), 1.75 (9H, s, $(\text{CH}_3)_2\text{C}=\text{CCH}_3$), 1.95 (1H, m, CHMe_2), 3.2 (1H, d, $J=10$ Hz, CHCN); MS *m/e*: 151

(M^+).

2-Isopropyl-3,4-dimethyl-3-pentenoic acid (14). A mixture of the nitrile **13** (900 mg), potassium hydroxide (1.5 g) and ethylene glycol (5 ml) was heated at 140°C under stirring for 20 hr. The solution was poured into water and washed with ether, and the aqueous layer was acidified with 5% HCl aq soln. The aqueous solution was extracted with ether three times and the extract was dried over Na_2SO_4 . Evaporation of the solvent gave 420 mg (41.5%) of **14**, n_D^{20} 1.4663; IR ν_{max} cm^{-1} : 3000~2500, 1705, 940; PMR (100 MHz, CDCl_3) δ : 0.75 and 1.0 (each 3H, d, $J=7$ Hz, $\text{C}(\text{CH}_3)_2$), 1.6 (3H, s, CH_3), 1.68 (3H, s, CH_3), 1.76 (3H, s, CH_3), 2.1 (1H, m, CHMe_2), 3.1 (1H, d, $J=11$ Hz, CHCOOH), 10.1 (1H, bs, COOH).

The acids **1**, **2**, **3**, **5**, **6** and **14** were converted to the corresponding acyl chlorides and esterified with 3-phenoxybenzyl alcohol by the usual method to give the esters **15**, **16**, **17**, **18**, and **19**. The products were purified by silica-gel chromatography.

3-Phenoxybenzyl 2-(2,2-dichloro-3-methylcyclopropyl)-3-methylbutyrate (20). The ester **16** (2 g) was added to the solution of benzyltriethylammonium chloride (0.2 g) in chloroform (30 ml) under stirring and then 50% NaOH aq soln (20 ml) was added to the mixture at room temperature. The solution was stirred for 72 hr at room temperature. Then the solution was poured into water and the chloroform layer was washed with dil HCl, brine and dried over MgSO_4 . The solvent was evaporated and the residue was chromatographed on silica gel (*n*-hexane) to give 2.10 g (83.6%) of the dichloride **20**, n_D^{25} 1.5412; IR ν_{max} cm^{-1} : 3070, 3040, 1740; PMR (60 MHz, CCl_4) δ : 0.95 (6H, d, $J=6$ Hz, $\text{C}(\text{CH}_3)_2$), 1.3 (3H, bs, CH_3), 1.7~2.4 (4H, m, $\text{CH} \times 4$), 5.15 (2H, s, CH_2), 6.8~7.6 (9H, m, PhH).

3-Phenoxybenzyl 2-(2,2-dichloro-3-ethylcyclopropyl)-3-methylbutyrate (21). The ester **17** (1 g), benzyltriethylammonium chloride (0.1 g), CHCl_3 (15 ml) and 50% NaOH aq soln (10 ml) were treated as described for **20** to give 0.85 g (68.2%) of **21**, n_D^{25} 1.5404; IR ν_{max} cm^{-1} : 1740; PMR (60 MHz, CCl_4) δ : 0.9~1.3 (9H, m, $\text{CH}_3 \times 3$), 1.4~2.3 (6H, m, $\text{CH} \times 4$ and CH_2CH_3), 5.15 (2H, s, CH_2), 6.8~7.6 (9H, m, PhH).

3-Phenoxybenzyl 2-isopropyl-3,4-epoxypentanoate (22). Ice-cooled *m*-chloroperbenzoic acid (0.8 g) in dichloromethane (15 ml) was added to a mixture of the ester **16** (1 g), sodium bicarbonate (0.75 g) and Na_2HPO_4 (0.15 g) in dichloromethane (10 ml) under stirring. After the mixture was stirred overnight at room temperature, sat. sodium bicarbonate was added to the solution and the solution was extracted with dichloromethane. The extract was washed with sodium bicarbonate soln, brine and dried over MgSO_4 . The solvent was evaporated and the residue was chromatographed on silica gel (Mallinkrodt CC-7)

(benzene-ether 3:1) to give 0.93 g (89%) of the epoxide **22**, n_D^{25} 1.5353; PMR (60 MHz, CCl_4) δ : 0.88 and 0.99 (each 3H, d, $J=3$ Hz, $\text{C}(\text{CH}_3)_2$), 1.25 (3H, d, $J=6$ Hz, CCH_3), 1.5~2.5 (2H, m, CHCO_2 and CHMe_2), 2.6~2.9 (2H, m,

$\begin{array}{c} \diagup \text{O} \diagdown \\ \text{HC}-\text{CH} \end{array}$, 5.1 (2H, s, CH_2), 6.5~7.7 (9H, m, PhH).

3-Phenoxybenzyl 2-isopropyl-3,4-epoxyhexanoate (23). Phenoxybenzyl hexenoate (**17**, 1 g) and *m*-chloroperbenzoic acid (0.8 g) were treated as described for **22** to give 0.92 g (88%) of **23**, n_D^{25} 1.5313; IR ν_{max} cm^{-1} : 1740, 1590, 1490, 1275, 1230, 900, 700; PMR (60 MHz, CCl_4) δ : 0.8~1.1 (9H, m, $\text{CH}_3 \times 3$), 1.2~2.1 (4H, m, CH_2CH_3 , CHCO_2 and CHMe_2), 2.4~2.9 (2H, m, $\begin{array}{c} \diagup \text{O} \diagdown \\ \text{HC}-\text{CH} \end{array}$), 5.1

(2H, s, CH_2), 6.6~7.7 (9H, m, PhH).

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