Syntheses of Novel Acetylene Cyclopropanes

Julia and Martel have reported the synthesis of chrysanthemate by the reaction of 3,3-dimethyl-2-propenyl phenyl sulfone with senecioate derivatives, independently.¹⁾ While, we have investigated intensively the nucleophilic reactions of acetylene sulfonium²⁾ and sulfonyl³⁾ ylids. In this paper we extended the reactions of acetylene sulfonium ylids with electrophiles to α,β -unsaturated esters.

The mixture of 3-phenyl-2-propynyl sulfonium salts (I) and methyl acrylate was treated with sodium hydride. Anusual work-up and dry column chromatography⁴⁾ on silica gel gave two kinds of cyclopropane derivatives each of which was composed of two stereoisomers. The sturcture of the major component (ca. 90%) of the first was assigned to methyl *trans*-2-phenethynylcyclopropane carboxylate (IIa): $C_{13}H_{12}O_2$; ⁵⁾ Mass Spectrum $m/e=200(M^+)$; UV: 249 nm ($\log \epsilon=4.31$); IR: 2235, 1733 cm^{-1} ; NMR⁶⁾ δ ppm: 1.35 (2H, m), 2.05 (2H, m), 3.70 (3H, s). The configuration of IIa was deduced to be *trans* from the predominant formation of the *trans*-cyclopropanes in the reaction of carbonyl-stabilized sulfonium ylids with α,β -unsaturated esters.⁷⁾ The major component (ca. 60%) of the second was assigned to methyl 1-phenethynyl-1-(2-methoxycarbonyl)-ethylcyclopropane carboxylate (IIIa): $C_{17}H_{18}O_4$; Mass Spectrum $m/e=286(M^+)$; UV: 249 nm ($\log \epsilon=4.30$); IR: 2230, 1740, 1734 cm^{-1} ; NMR δ ppm: 1.0-2.9 (7H, m), 3.67 (3H, s), 3.75 (3H, s). The protons on the cyclopropane ring of IIIa were assignable using a shift reagent⁶⁾: 2.40 (1H, dd, Ha), 3.57 (1H, dd, Hb), 4.15 (1H, dd, Hc): $J_{ab}=4.5Hz$, $J_{bc}=6.5$, $J_{ca}=8.3$.

Acetylene sulfonium ylids are liable to produce allenic sulfides by 1,5-sigmatropic rearrangement.⁸⁾ In order to avoid this, 3-phenyl-2-propynyl sulfonium salts derived from tetramethylene sulfide or pentamethylene sulfide in place of dimethyl sulfide were chosen. In fact Ib and Ic afforded better results than Ia.

An independent synthesis of II was proceeded as shown in Chart 1 (IV $\rightarrow$ V $\rightarrow$ VI $\rightarrow$ II). Determination of the configuration of IIa was based on the degradation. The partial hydrogenation of IIa using 5% Pd/CaCO₃ (in MeOH-quinoline) gave VII ($M^+=202$, $\nu_{C=O}=1730\text{ }cm^{-1}$, $\delta=6.42$ ppm: 1H, d, $J_1=11.5Hz$, 5.07 ppm: $J_1=11.5Hz$, $J_2=9.0$), which was successively treated with OsO₄ and NaIO₄. The reaction mixture, which comprised benzaldehyde and methyl *trans*-2-formylcyclopropanecarboxylate, was converted directly to two esters according to Corey's method,⁹⁾ methyl benzoate and dimethyl *trans*-1,2-cyclopropanedicarboxylate. The scope and limitation are summarised in Table I.

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TABLE I

Rnu	IX	R ₁	R ₂	R ₃	Yield (%)	bp(mm Hg) (mp)	mp of -CO ₂ H
1	MA	Ph	H	H	75	108–110 (0.3)	89– 90 (<i>trans</i>) 84– 85 (<i>cis</i>)
2	MC	Ph	Me	H	11	110–115 (0.2)	
3	MS	Ph	Me	Me	trace		
4	MF	Ph	CO ₂ Me	H	19	150–155 (0.01)	205–207 (<i>trans</i>)
5	MM	Ph	H	CO ₂ Me	25	150–155 (0.01)	205–207 (<i>trans</i>)
6	MA	<i>p</i> -tolyl	H	H	43	112–113 (10 ⁻³)	95– 96
7	MA	<i>p</i> -Br-Ph	H	H	56	(57–59) (<i>trans</i>)	122–124 (<i>trans</i>)
8	MCi	<i>p</i> -Br-Ph	Ph	H	4		
9	MA	Me	H	H	57	108–110 (50)	87– 88
10	MC	Me	Me	H	33	106–108 (30)	54– 56
11	MA	H	H	H	6		

MA: methyl acrylate, MF: methyl fumarate, MC: methyl crotonate, MM: methyl maleate, MS: methyl senecioate, MCi: methyl cinnamate

Central Research Laboratories,
Sankyo Co., Ltd.
Hiromachi, Shinagawa-ku, Tokyo

MASAFUMI YOSHIMOTO
NOBORU ISHIDA
YUKICHI KISHIDA

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Reaction of N-(1-Cyanoalkyl)alkylideneamine N-Oxide with Carboxamides

It is known that nitrones react as a 1,3-dipole with many unsaturated compounds to give cycloadducts, and with Grignard reagents and hydrogen cyanide to give hydroxylamines.¹⁾

However, all these reactions, except the cycloadditions of isocyanate, isothiocyanate,¹⁾ and N-sulfinylaniline,²⁾ involve a carbon nucleophile which attacks on the carbon atom of a nitrone group.

In this communication, we wish to report the first example of a non-cyclic 1,3-addition reaction of a nitrogen nucleophile with a nitrone.

When N-(1-cyanoalkyl)alkylideneamine N-oxide was dissolved in excess formamide at room temperature and the mixture was allowed to stand for 3—10 days, a crystalline product, consistent with the expected 1:1 adduct (I), was separated from the solution.

TABLE I. N-(1-Cyanoalkyl)N-(1'-carbonamidoalkyl) Hydroxylamine

(I)	R ¹	R ²	R ³	mp (°C)	Formula	Analysis (%)					
						Calcd.			Found		
						C	H	N	C	H	N
a	Pr ⁿ	Pr ⁱ	H	148.5—149.0	C ₁₀ H ₁₉ O ₂ N ₃	56.38	8.99	19.73	56.29	8.98	19.58
b	Pr ⁿ	Pr ⁿ	H	145.0—146.5	C ₁₀ H ₁₉ O ₂ N ₃	56.38	8.99	19.73	56.56	8.83	19.77
c	Pr ⁱ	Pr ⁿ	H	134.0—135.0	C ₁₀ H ₁₉ O ₂ N ₃	56.38	8.99	19.73	56.14	8.91	20.02
d	Pr ⁱ	Pr ⁱ	H	121.5—122.0	C ₁₀ H ₁₉ O ₂ N ₃	56.38	8.99	19.73	56.51	8.91	19.46
e	Pr ⁿ	Et	H	151.5—152.0	C ₉ H ₁₇ O ₂ N ₃	54.32	8.61	21.12	54.10	8.55	21.71
f	Pr ⁱ	Et	H	138.0—139.0	C ₉ H ₁₇ O ₂ N ₃	54.32	8.61	21.12	54.21	8.52	20.71
g	Et	Pr ⁿ	H	140.0—140.5	C ₉ H ₁₇ O ₂ N ₃	54.32	8.61	21.12	54.48	8.59	21.05
h	Et	Pr ⁱ	H	154.0—154.5	C ₉ H ₁₇ O ₂ N ₃	54.32	8.61	21.12	54.21	8.65	21.16
i	Pr ⁱ	Me	H	137.0—137.5	C ₈ H ₁₅ O ₂ N ₃	51.87	8.16	22.69	52.16	8.44	22.69
j	Pr ⁱ	Pr ⁱ		155.5—156.0	C ₁₅ H ₂₂ O ₂ N ₄	62.12	7.65	19.32	61.91	7.55	19.13
k	Pr ⁱ	Pr ⁱ		146.0—148.0	C ₁₅ H ₂₂ O ₂ N ₄	62.12	7.65	19.32	62.24	7.47	19.37
l	Pr ⁿ	Pr ⁱ		150.0—150.5	C ₁₅ H ₂₂ O ₂ N ₄	62.12	7.65	19.32	61.81	7.62	18.98

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