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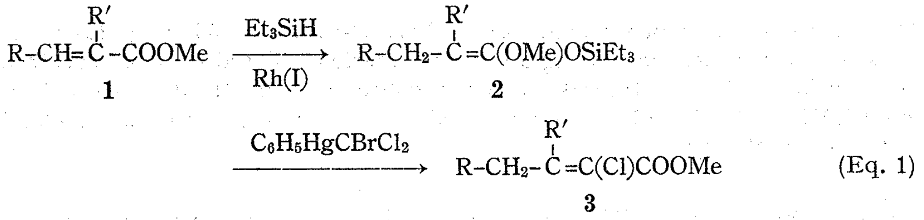
α-Chlorinative Homologation of α,β-Unsaturated Esters

Ketene triethylsilyl methyl acetals obtained by hydrosilation of α,β-unsaturated esters were reacted with phenyl(bromdichloromethyl)mercury to give homologated 2-chloroacrylates

Recently we reported an effective preparative method of ketene silyl alkyl acetals (2) by $[(C_6H_5)_3P]_3C_6H_5Cl$ catalyzed hydrosilation of α,β-unsaturated esters (1).[1] The uses of this group of compounds as synthetic intermediates have been demonstrated by several workers[2] since Ainsworth, *et al.*[3] had prepared them by silylating the enolate of saturated esters.

This communication describes the dichlorocarbene addition of the ketene triethylsilyl methyl acetals obtained from α,β-unsaturated esters (Eq. 1). The reaction of 2 with phenyl(bromodichloromethyl)mercury was effected in refluxing benzene or dimethoxyethane and produced unsaturated α-chloroesters (3) presumably *via* thermally unstable dichlorocyclopropane derivative.[4] The yield and physical data of 3 are given in Table I.



$$\underset{\mathbf{1}}{\mathrm{R\text{-}CH{=}\overset{R'}{C}\text{-}COOMe}}\ \xrightarrow[\mathrm{Rh(I)}]{\mathrm{Et_3SiH}}\ \underset{\mathbf{2}}{\mathrm{R\text{-}CH_2\text{-}\overset{R'}{C}{=}C(OMe)OSiEt_3}}\ \xrightarrow{\mathrm{C_6H_5HgCBrCl_2}}\ \underset{\mathbf{3}}{\mathrm{R\text{-}CH_2\text{-}\overset{R'}{C}{=}C(Cl)COOMe}} \qquad \text{(Eq. 1)}$$

Chart 1

TABLE I. α-Chloro-α,β-unsaturated Esters[a] obtained by the Reaction of 2 and Phenyl(bromodichloromethyl)mercury

Compd.	R	R'	Yield(%)[b]	bp, °C(Torr)[c]	NMR: δ_{ppm} in CCl_4 (J in Hz)	IR (film) cm^{-1}
3a	H	H	80	80(17)	2.19(s), 2.04(s), 3.74(s)	1720, 1616
3b[d,e]	Me	H	63	80(20)	1.13(t, $J=7.5$), 2.38(quintet, $J=7.5$) 3.78(s), 6.98(t, $J=7.5$)	1720, 1626
3c[e,f]	Me	Me	92	120(18)	2.15(s, *Z*-isomer), 2.00(s, *E*-isomer) 3.75(s)	1715, 1610
3d[d,e]	C_6H_5	H	52	120 (1)	3.67(*d*, $J=7.5$), 3.80(s), 7.17(br. s)	1730, 1630

a) All compounds gave satisfactory elemental analyses.
b) The yields based on 2 determined by vpc using internal standards and not optimized
c) Temperatures indicate bath temperatures.
d) *Z*-isomer
e) The geometrical isomerism was determined by correlating the chemical shifts of β-substituents: C. Pascual, J. Meier, and W. Simon, *Helv. Chim. Acta*, 49, 164 (1966)
f) *E*, *Z*-Mixture in the ratio of 1: 2. The ketene acetal derived from methyl tiglate was used.

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2) Y-N. Kuo, F. Chen, and C. Ainsworth, *J. Am. Chem. Soc.*, **93**, 4604 (1971); P.L. Creger, *Tetrahedron Lett.*, **1972**, 79; M.W. Rathke and D.F. Sullivan, *ibid.*, **1973**, 1927; R.H. Reuss and A. Hassner, *J. Org. Chem.*, **39**, 1785 (1974); J.K. Ramusen and A. Hassner, *ibid.*, **39**, 2558 (1974); K. Saigo, M. Osaki, and T. Mukaiyama, *Chemistry Letters*, **1975**, 989.
3) C. Ainsworth, F. Chen, and Y-N. Kuo, *J. Organometal. Chem.*, **46**, 59 (1972).
4) Formation of 2,2-dichlorocyclopropanone acetals by the addition of dichlorocarbene to ketene dialkylacetals has been reported. S.M. McElvain and P.L. Weyna, *J. Am. Chem. Soc.*, **81**, 2579 (1959).

The reaction sequence presented here provides a methodology for the homologation of α,β-unsaturated esters with simultaneous introduction of α-chlorine atom, though the limitation exists in the case of β,β-disubstituted **1** where hydrosilation failed, probably due to steric hindrance.[5]

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[5] Our unpublished results.

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Sulfur-containing Metabolites of 2,5,2',5'-Tetrachlorobiphenyl, a Major Component of Commercial PCB's

The excretion of four new metabolites of 2,5,2',5'-tetrachlorobiphenyl (TCB) in mice feces was revealed by gas chromatographic examination. Based on mass spectrometric data and syntheses, the structures of these metabolites were identified as 3- and 4-methylsulfonyl-2,5,2',5'-TCB (I and II, respectively), and 3- and 4-methylthio-2,5,2',5'-TCB (III and IV, respectively).

Since polychlorobiphenyls (PCB's) were recognized as one of the most widespread pollutants in the environment, a number of studies on the metabolic fate of individual chlorobiphenyl isomers have been undertaken. Hydroxylation is now well known as the major metabolic reaction among most of the chlorobiphenyls tested.[1]

During the course of a thorough gas chromatographic examination of the fecal excreta of mice given 2,5,2',5'-tetrachlorobiphenyl (TCB), we have found the presence of four nonpolar metabolites. This paper deals with the structural elucidation of these novel metabolites.

2,5,2',5'-TCB was dissolved in vegetable oil and intraperitoneally administered (8 mg/animal) to female dd strain mice weighing 19—21 g. The feces were collected for 6 days after administration of the material. The feces were dried and extracted with benzene in a Soxhlet apparatus. The benzene extracts were chromatographed on a silica gel dry column, and divided into three fractions: fraction 1, eluted with 10 ml of hexane; fraction 2, eluted with 6 ml of benzene; and fraction 3, eluted with further 10 ml of benzene. Each of the fractions was analysed using a gas chromatograph equipped with an electron capture detector and a combined gas chromatograph–mass spectrometer. Fraction 1 contained unchanged 2,5,2',5'-TCB. Both fractions 2 and 3 contained two metabolites, A and B, and C and D, respectively (Fig. 1).

The mass spectra of both metabolites C and D (Fig. 2) showed molecular ion at m/e 368, corresponding to an elemental composition $C_{13}H_8O_2Cl_4S$ (based on high-resolution measure-

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[1] *a*) H. Yoshimura and H. Yamamoto, *Chem. Pharm. Bull.* (Tokyo), **21**, 1168 (1973); *b*) H. Yoshimura, H. Yamamoto, and S. Saeki, *ibid.*, **21**, 2231 (1973); *c*) A.M. Gardner, J.T. Chen, J.A.G. Roach, and E.P. Ragelis, *Biochem. Biophys. Res. Commun.*, **55**, 1377 (1973); *d*) S. Jensen and G. Sundström, *Nature*, **251**, 219 (1974); *e*) I.C. Hsu, J.P. Van Miller, and J.R. Allen, *Bull. Environ. Contam. Toxicol.*, **14**, 233 (1975); *f*) H. Yoshimura, H. Yamamoto, and K. Yonezawa, *Fukuoka Igaku Zasshi*, **66**, 555 (1975) and the references cited therein.