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A LIMITATION OF TRICHLOROETHOXYCARBONYL CHLORIDE AS AN ACYLATING REAGENT

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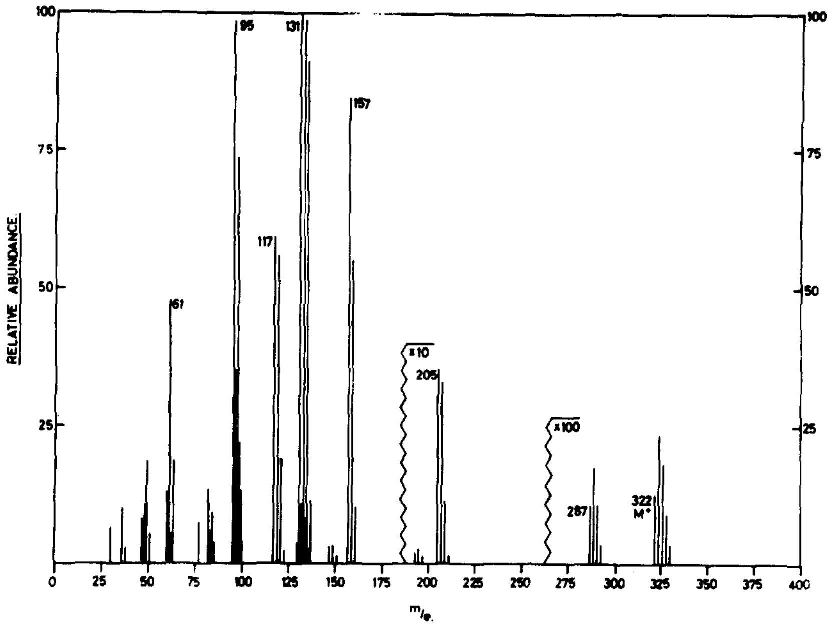
Windholz & Johnson (1) have recently described the use of βββ-trichloroethoxycarbonyl chloride as an acylating reagent for hydroxyl and amino groups under mild conditions. The present note reports certain limitations in the former case.

The presence of the $-CCl_3$ group, long known as a vital portion of several important fungicidal compounds (2) made $Cl_3C.CH_2.O.COCl$ attractive in connection with work on the synthesis of potential fungicides for the control of powdery mildews. Accordingly attempts were made to prepare 4-cyclohexyl-, 4-(cyclopentylmethyl)- and 4-(1-cyclobutylhexyl)-2,6-dinitrophenyl trichloroethyl carbonates using the method outlined (1). In each case the same product was obtained and crystallised from light petroleum (b.p. 40-60°), m.p. 91-92°. (Found: C, 18.9; H, 1.2. Calc. for $C_5H_4O_3Cl_6$: C, 18.5; H, 1.2%). ν_{max}(cm^{-1}) 3020, 2975, 2460 (CH_2 str.), 1765 (C = O str.) 1280, 1230 (ester). The proton magnetic resonance spectrum showed only a singlet at 5.25 τ (3). The mass spectrum is shown in the figure and the relative abundance ratios of the isotopic peaks of the molecular ion cluster showed the presence of five or more chlorine atoms in the molecule. Structures for the main fragment ions are suggested below and these data are consistent with the unknown being bis-trichloroethyl carbonate.

m/e	Fragment ion
322 (M^+)	$(Cl_3C.CH_2.O.CO.O.CH_2.CCl_3)^+$
287	$Cl_2C^+.CH_2.O.CO.O.CH_2.CCl_3$
205	$H_2C^+.O.CO.O.CH_2.CCl_3$
157	$Cl_2C^+.CH_2.O.CO.OH$
131	$Cl_3C.C^+H_2$
117	C^+Cl_3
95	$Cl_2C = C^+H$
61	$O^+.CO.OH$

An authentic specimen of bis-trichloroethyl carbonate prepared from βββ-trichloroethanol and phosgene (4) gave identical i.r., p.m.r. and mass spectra.

This compound was also obtained in 84% yield by stirring a solution of $Cl_3C.CH_2.O.COCl$ in pyridine at room temperature overnight, and as a substantial by-product in the preparation of p-chlorophenyltrichloroethyl carbonate using this reagent, both in the presence of pyridine or when Schotten-Baumann conditions were employed. p-Chlorophenyl trichloroethyl carbonate crystallised from light petroleum (b.p. 40–60°), m.p. 66–67° (Found: C, 35.6; H, 2.4. $C_9H_6O_3Cl_4$ requires C, 35.4; H, 2.0%). ν_{max}(cm^{-1}) 1780, 1285, 1225 (ester), 1500 (C–C aromatic) 820 (2 free H) 740, 720 (C–Cl). The p.m.r. spectrum showed a singlet at 5.25 τ and a multiplet at 2.7τ.



Mass spectrum of bis-trichloroethyl carbonate

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References

1. T. B. Windholz & D. B. R. Johnston, Tetrahedron Letters, No.27, 2555 (1967).
2. D. Woodcock, Chem. Brit., 4, 294 (1968).
3. Determined on a Varian HA-100 in $CDCl_3$ using TMS as internal standard.
4. J. V. Swintosky, N. J. Adams, H. C. Calderwell, L. W. Dittert, T. Ellison & D. E. Rivard, J. Pharm. Sci., 55, 992 (1966).