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Preliminary Note

The generation of fluorocarboethoxycarbene by the organomercury procedure

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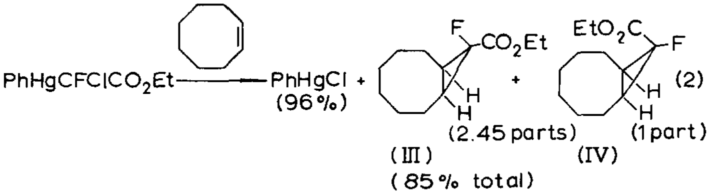
The known fluorocarbenes (exclusive of CF_3-substituted species) include CF_2, CFCl, CFBr, CFH, FCOMe, FCCN, $FCNF_2$, FCPh and $FCCHF_2$[1]. These species are useful reagents for the synthesis of fluorine-containing cyclopropanes by reaction with olefins and it would be desirable to enlarge this list by addition of other functional fluorocarbenes. We report here concerning a new carbene of this type, fluorocarboethoxycarbene, $FCCO_2Et$.

Organomercury reagents have served well in the generation of CF_2[2], CFCl[3] and CFBr[4], and we have used an organomercury intermediate for the generation of $FCCO_2Et$. In earlier work[5,6], we had prepared $PhHgCCl_2CO_2Me$, $PhHgCClBrCO_2Me$ and $PhHgCBr_2CO_2Me$ by the procedure shown in equation (1).

$$PhHgCl + HCX_2CO_2Me + Me_3COK \xrightarrow[\text{low temp.}]{\text{THF}} PhHgCX_2CO_2Me + KCl + Me_3COH \qquad (1)$$

Our successful preparation of $PhHgCFClCO_2Et$ was based on a report by Knunyants *et al.*[7] concerning the synthesis of $Hg(CFClCO_2Et)_2$ (I) and $ClHgCFClCO_2Et$ (II). As these workers found, the reaction of mercuric nitrate with $CClF{=}CFOEt$[8] in absolute ethanol, followed by treatment with mercuric chloride, gave a mixture of (I) and (II), isolated as a heavy oil. However, we found that this mixture can be converted easily to $PhHgCFClCO_2Et$ by reaction with diphenylmercury in benzene. In practice, an aliquot of the benzene solution of (I) and (II) is "titrated" with a benzene solution of diphenylmercury until no additional phenylmercuric chloride precipitates. With this $[(I)+(II)]/Ph_2Hg$ ratio thus established, the conversion to $PhHgCFClCO_2Et$ on a preparative scale can be undertaken. The $PhHgFClCO_2Et$ produced can be isolated in good purity (m.p. 98–105°) by filtration of the PhHgCl and evaporation of the filtrate. A yield of 67%, based on mercuric nitrate charged, is typical. A sample of product recrystallized from dichloromethane–hexane, with m.p. 101–105°, was of analytical purity; ^1H NMR ($CDCl_3$): δ 1.33 (t, $J = 7$ Hz, 3H, $OCH_2C\underline{H_3}$), 4.35 (q, $J = 7$ Hz, 2H, $OC\underline{H_2}CH_3$) and 7.13–7.47 ppm (m, 5H, Ph); IR (CCl_4): $\nu(C{=}O)$ 1758, 1730 cm^{-1}.

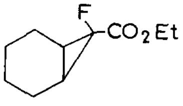
The $PhHgCFClCO_2Et$ thus prepared was found to be an effective $FCCO_2Et$ transfer agent. Thus its reaction under nitrogen with an excess of cyclo-octene (no solvent) at ~ 145° for 36 h gave the results shown in equation (2).



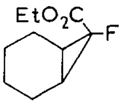
The assignment of the structures shown for isomers (III) (n_D^{25} 1.4699) and (IV) (n_D^{25} 1.4652) was based on the fact that in fluorocyclopropanes $J(H\text{–}F)_{cis} > J(H\text{–}F)_{trans}$[9]. In the ^{19}F NMR spectrum (at 56.446 MHz) of (IV) (in acetone solution), the fluorine signal appeared as a triplet ($J = 23.6$ Hz) at 11.3 ppm upfield from internal C_6F_6. The corresponding fluorine signal of (III) appeared as a singlet at 57.0 ppm with a half-height width of 8.5 Hz*.

The yield of the (III) + (IV) product mixture obtained under standard conditions (~ 136° for 18 h) was not diminished upon change of the reaction medium from neat olefin to 1:1 olefin/chlorobenzene to 1:6 olefin/chlorobenzene, which suggests that a carbene mechanism is indeed operative.

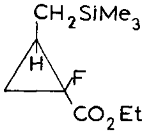
The reaction of $PhHgCFClCO_2Et$ with an excess of cyclohexene (sealed tube, 133°, 24 h) gave a 2.4:1 mixture of (V) and (VI) in 55% yield, and this mercurial reacted with allyltrimethylsilane (sealed tube, 133° for 62 h) to give a 1.9:1 mixture of (VII) and (VIII) in 44% yield. Insertion of $FCCO_2Et$ into the Si–H bond of triethylsilane also could be effected (eq. (3)).



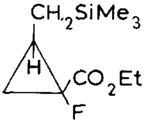
(V)



(VI)



(VII)



(VIII)

$$PhHgCFClCO_2Et + \underset{(excess)}{Et_3SiH} \xrightarrow{110°,\ 50\ h} \underset{(71\%)}{Et_3SiCHFCO_2Et} + PhHgCl \qquad (3)$$

The isolated yield of phenylmercuric chloride was only 25%, since under these reaction conditions its reduction by triethylsilane to give elemental mercury (54%), benzene and triethylchlorosilane (44%) occurred. The structure indicated for the organosilicon product in equation (3) is supported by occurrence of H–F spin–spin coupling (^1H NMR (CCl_4) shows $SiC\underline{H}F$ at δ 4.82 ppm as a doublet, J (H–F = 47.2 Hz) and strong C=O bands in the IR spectrum (liquid film) at 1752 and 1719 cm^{-1}.

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* Note a similar situation in the case of the *syn* and *anti* isomers of 7-fluoro-7-phenylnorcarane[10].

Our studies of the chemistry of fluorocarboethoxycarbene are continuing and full details will be reported at a later date.

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REFERENCES

1 W. A. Sheppard and C. M. Sharts, *Organic Fluorine Chemistry*, Benjamin, New York, 1969, Ch. 6, Sect. 1B, in particular Table 6-2.

2 (a) D. Seyferth, S. P. Hopper and K. V. Darragh, *J. Amer. Chem. Soc., 91* (1969) 6536.
(b) D. Seyferth and S. P. Hopper, *J. Organometallic Chem., 26* (1971) C62.

3 D. Seyferth and K. V. Darragh, *J. Org. Chem., 35* (1970) 1297.

4 D. Seyferth, C. K. Haas and S. P. Hopper, *J. Organometallic Chem., 33* (1971) C1.

5 D. Seyferth, D. C. Mueller and R. L. Lambert, Jr., *J. Amer. Chem. Soc., 91* (1969) 1562.

6 D. Seyferth, R. A. Woodruff, D. C. Mueller and R. L. Lambert, Jr., *J. Organometallic Chem.*, in press.

7 V. R. Polishchuk, L. S. German and I. L. Knunyants, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, (1971) 2024.

8 S. Dixon, *J. Org. Chem., 21* (1956) 400.

9 K. L. Williamson, Y.-F. Li, F. H. Hall and S. Swager, *J. Amer. Chem. Soc., 88* (1966) 5678.

10 T. Ando, Y. Kotoku, H. Yamanaka and W. Funusaka, *Tetrahedron Letters*, (1968) 2479.