Tetrahedron Letters No.36, pp. 3909-3910, 1968. Pergamon Press. Printed in Great Britain.

PERFLUORO(METHYLACETYLENE)

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(Received in UK 6 June 1968; accepted for publication 13 June 1968)

Hitherto no perfluoroalkynes of type $R_F.C\vdots CF$ (where R_F = F, perfluoroalkyl, or perfluoroaryl) have been isolated and characterised. The simplest member of the series in which R_F= perfluoroalkyl, namely perfluoro(methylacetylene), has now been synthesised by the two routes shown below. It is a colourless gas, b.p. -50°, which undergoes no change when stored in glass at 25°/10 cm.Hg for 1 month or 20°/1.25 atm. for 4 days; it slowly polymerizes to a waxy solid when kept at higher pressures so that a liquid phase is present. This and other reactions of the acetylene are currently under investigation. The acetylene reacts rapidly with electron-rich dienes (e.g., cyclopentadiene), and is susceptible towards nucleophilic attack; thus it is slowly destroyed by water at room temperature and reacts with potassium fluoride in formamide:

$$CF_3.C\vdots CF \xrightarrow{F^-} CF_3.\bar{C}{:}CF_2 \xrightarrow{\text{Solvent}} CF_3.CH{:}CF_2$$

No explosion hazards have yet become apparent (cf. monofluoroacetylene,[1] which is treacherously explosive in the liquid state).

Route A

$$CF_2Br_2 + CH_2{:}CF_2 \xrightarrow[110^\circ]{(PhCO)_2O_2} CF_2Br.CH_2.CF_2Br\ (62\%) \xrightarrow[300^\circ/1\ mm.Hg]{C/SiO_2}$$

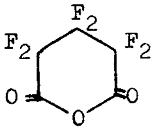
$$CF_2Br.CH{:}CF_2\ (86\%) \xrightarrow[34^\circ/light]{Br_2} CF_2Br.CHBr.CF_2Br\ (92\%) \xrightarrow[20^\circ/40\ mm.Hg]{50\%\ KOH\ aq.}$$

$$CF_2Br.CBr{:}CF_2\ (91\%) \xrightarrow[-196\ to\ 20^\circ]{AlBr_3} CF_3.CBr{:}CFBr\ (97\%) \xrightarrow[reflux]{Zn,\ dioxan}$$

(cis:trans = 60:40)

$$CF_3.C{\vdots}CF\ (43\%)$$

Route B



$$\xrightarrow[420^\circ/1\text{-}2\ mm.Hg]{KF} [CF_2{:}CF.CF_2.COF] \xrightarrow{F^-} CF_3.CF{:}CF.COF\ (26\%)$$

(cis:trans = 45:55)

$$\xrightarrow{NaOH} CF_3.CF{:}CF.CO_2Na\ (86\%) \xrightarrow{220\text{-}240^\circ} CF_3.C{\vdots}CF\ (26\%)$$

The identities of the intermediates in the above routes were established by elemental analysis and spectroscopic methods. Perfluoro(methylacetylene) absorbs strongly in the infrared at 4.24μ (C⋮C str.), and its ^{19}F n.m.r. spectrum (35°/56.46 Mc./sec.) shows two absorptions [$\phi^*_{CF_3}$ 50.8 (doublet); ϕ^*_F (quartet) 203.0; $|J_{FF}|$ 4.3 c./sec.] with relative intensity 3:1 [for the ^{13}C satellites of the ϕ^*50.8 doublet $|J_{CF}|$ = 259.0 (δ_{CF}= +0.132$\pm$0.005) and $|J_{CCF}|$ = 57.7 c./sec. (δ_{CCF}= 0.011$\pm$0.002 p.p.m.)].

[1] W.J.Middleton and W.H.Sharkey, J.Amer.Chem.Soc., 81, 803,(1959).