Diels–Alder Reactions involving Perfluorocyclopentadiene

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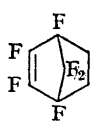
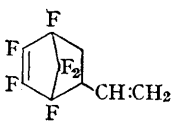
IN the Diels–Alder reaction, perfluorocyclopentadiene[1] acts (*a*) as a diene in its thermal reactions in sealed vessels with ethylene [106°/8 days → I(51%) yield], butadiene [110°/4·5 days → II (64%) + III(< 1%)], norbornadiene [102°/6 days → IV(77%)], maleic anhydride [110°/3 days → V(41%)], dimethyl acetylenedicarboxylate [130°/3 days → VI(22%)], or trifluoronitrosomethane



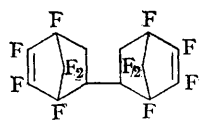
(I)

b.p. 107-108°/767mm.



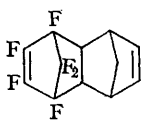
(II)

b.p. 132°



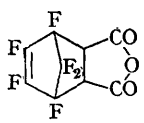
(III)

m.p. 167-168°



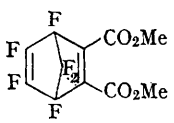
(IV)

Two stereoisomers
b.p. 190°/772 mm. and
m.p. 98·5-101°, respectively



(V)

m.p. 164-165·5°

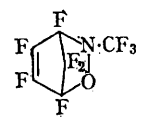


(VI)

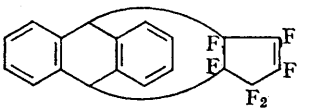
m.p. 49-50°

[20°/1 day → VII(98%)], but (*b*) as a dienophile when heated with anthracene [120°/5 days → VIII(23%)] and (*c*) as both a diene and a dienophile when heated with cyclopentadiene [80°/10 min. → IX(17%) + X(70%). Like cyclopentadiene, perfluorocyclopentadiene readily dimerises[1] by a Diels–Alder reaction [120°/1 day → XI(87%)], but even under forcing conditions (100–300°/1–2·5 days, autoclave) it does not appear to combine with tetrafluoroethylene, tetracyanoethylene, or perchlorocyclopentadiene. Thus, perfluorocyclopentadiene reacts more like perchlorocyclopentadiene,[2] and markedly different from perfluorobutadiene. The last compound does not participate in a normal Diels-Alder reaction, but reacts thermally with certain dienes or dienophiles to give cyclobutane derivatives[3] [*e.g.*, (XII) with acrylonitrile], and dimerises thermally to give perfluoro(tricyclo[3,3,0,$0^{2,6}$]octane) (XIII).[4]

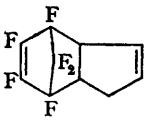
The structures of adducts (I)–(XI), which had correct elemental analyses, were determined by nuclear magnetic resonance spectroscopy, and where possible supporting evidence was obtained by chemical methods and by ultraviolet, infrared, and mass spectroscopy. For example, pyrolysis of (VI) gives dimethyl tetrafluorophthalate (34% yield), perfluorocyclobutane (35%), and traces of tetrafluoroethylene:



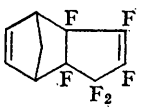
(VII)
b.p. 65-66·5°



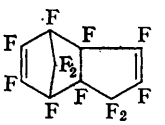
(VIII)
m.p. 145-147°



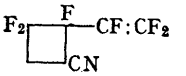
(IX)
m.p. 37-39·5°



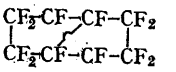
(X)
m.p. 23-25°



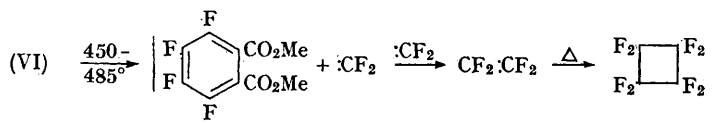
(XI)
m.p. 42·5-43°



(XII)



(XIII)



m.p. 71-73°

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[1] R. E. Banks, R. N. Haszeldine, and J. B. Walton, *J.*, 1963, 5581.
[2] H. E. Ungnade and E. T. McBee, *Chem. Rev.*, 1958, **58**, 249; J. Sauer and H. Wiest, *Angew. Chem.* (*Internat. Edn.*), 1963, 269; A. A. Danish, M. Silverman, and Y. A. Tajima, *J. Amer. Chem. Soc.*, 1954, **76**, 6144.
[3] R. M. Ryazanova, I. M. Dolgopol'skiĭ, and A. L. Klebanskiĭ, *Zhur. Vsesoyuz. Khim. Obshchestva im D. Z. Mendeleeva*, 1961, **6**, 356.
[4] I. L. Karle *et al.*, *J. Amer. Chem. Soc.*, 1964, **86**, 2523.