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TWO-WAY CYCLOADDITION OF FLUORO-OLEFINS TO PROPADIENE

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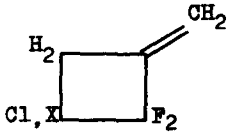
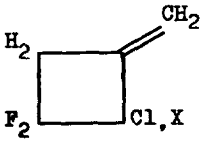
Cycloaddition reactions between an allene and a ketone or unsymmetrically substituted olefin $CH_2:CHX$ (where X = CN, CO_2H, CO_2CH_3, CHO, etc.) have hitherto been reported to give only one of the two possible 1:1 adducts, the structures of which were shown to be, respectively, 2-alkylideneoxetans (1) and 3-substituted methylenecyclobutanes (2). We have found that thermal co-dimerisation of propadiene with an unsymmetrical fluoro-olefin $CF_2:CClX$ (where X = F or Cl) gives both possible adducts (I a,b; II a,b).



(I: a, X=F; b, X = Cl)

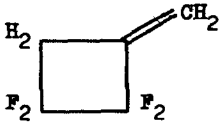


(II: a, X=F; b, X=Cl)

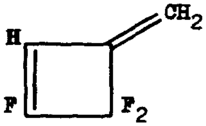
An approximately equimolar mixture of propadiene and chlorotrifluoroethylene, kept for 2 days at 150° under autogenous pressure, in the presence of a polymerisation inhibitor (Terpene B), gives an 85:15 mixture of Ia and IIa in 30% yield. A similar reaction between propadiene and 1,1-dichlorodifluoromethylene at 165° affords a 95:5 mixture of Ib and IIb in 75% yield.

The adduct mixtures were isolated from crude products by preparative gas-liquid chromatography (Perkin-Elmer F21 fractometer, operating with 2m. diethyleneglycol succinate and 3m. carbowax columns at 75°). The individual isomers were not resolved on the columns used, but the mixed 1:1 adducts gave correct combustion analyses and mass spectrometric molecular weights.

The structures of the major isomers (I a,b) were established by comparison of their ${}^{1}H$ n.m.r. (Table 1) and ${}^{19}F$ n.m.r. spectra (Table 2) with those of III, obtained by a similar reaction between propadiene and tetrafluoroethylene (3). Confirmatory evidence for Ia was obtained by its dehydrochlorination with anhydrous potassium hydroxide at 80°, which gave a 35% yield of 1,4,4-trifluoro-3-methylenecyclobutene (IV), identical with a sample obtained by similar dehydrofluorination of III.



(III)



(IV)

The compositions of the mixed 1:1 adducts were determined mainly from the relative intensities of the bands in their ${}^{19}F$ n.m.r. spectra (Table 2), but additional evidence was obtained from their mass spectra.

TABLE 1

^1H N.m.r. Spectra (60 Mc.sec.$^{-1}$, Shifts Relative to C_6H_6)

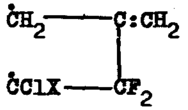
Methylene - cyclobutane	Band	Chemical Shift (p.p.m)	Multiplicity (J in c.sec.$^{-1}$)	Intensity	Assignment
III	1	1·1	Unresolved	1	Vinyl H
	2	1·4	Unresolved	1	Vinyl H
	3	3·8	Triplet (J_{HF}=12)	2	$CH_2 \cdot CF_2$
Ia	1	1·1	Unresolved	1	Vinyl H
	2	1·3	Unresolved	1	Vinyl H
	3	3·6	Doublet (J_{HF}=12)	2	$CH_2 \cdot CFCl$
IIa	1	0·7	Multiplet	1	Vinyl H
	2	1·1	Multiplet	1	Vinyl H
	3	3·2	Singlet	2	$CH_2 \cdot CCl_2$

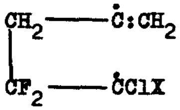
TABLE 2

^{19}F N.m.r. Spectra (56·46 Mc.sec.$^{-1}$, Shifts Relative to $CF_3 \cdot CO_2H$)

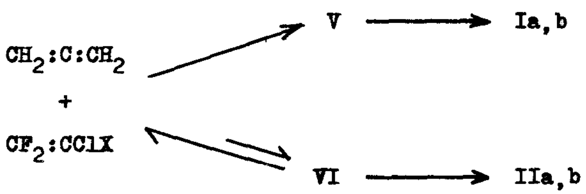
Methylene-cyclobutane	Band	Chemical Shift (p.p.m)	Multiplicity (J in c.sec.$^{-1}$)	Rel. Intensity (%)	Assignment
III	1	38·7	Singlet	50	$CF_2 \cdot CF_2$
	2	40·3	Triplet (J_{FH}=12)	50	$CF_2 \cdot CH_2$
Ia + IIa	1	29·9	AB (J=210)	57	CF_2 in Ia
	2	42·2	Triplet (J_{FH}=13)	28	CFCl in Ia
	3	32·0	AB (J=195)	10	CF_2 in IIa
	4	37·7	Singlet	5	CFCl in IIa
Ib + IIb	1	21·4	Triplet (J_{FH}=3)	95	CF_2 in Ib
	2	24·2	Triplet (J_{FH}=11)	5	CF_2 in IIb

Although a concerted four-centre mechanism for the co-dimerisation cannot be excluded, there is evidence that a two-step process is allowed in closely related 1,2-cycloadditions (4,5). Bond formation to these olefins should occur first at the difluoromethylene group; for example, less than 1% of 1,3-dichlorohexafluorocyclobutane is formed by thermal dimerisation of chlorotrifluoroethylene (6), and a variety of free-radicals attack these fluoro-olefins almost exclusively at the more fluorinated carbon atom (7,8). The most probable diradical intermediates are therefore V and VI, of which V leads to the main component of the 1:1 adduct mixtures.


(V)


(VI)

The predominance of products from V, which implies that initial bond formation is > 85% to the 2-position of propadiene, conflicts with the general pattern of free-radical additions to this allene (9). An alternative explanation, similar to that suggested previously to account for the effect of temperature and concentration on the rate of reaction of propadiene with thiyl radicals and bromine atoms (10), is that VI forms more rapidly than V, but dissociates preferentially, since it cannot achieve allylic stabilisation. Formation of V is in contrast essentially irreversible, because rapid 90° rotation about the $\dot{C}H_2$--$\dot{C}R_F{:}CH_2$ bond leads to allylic resonance.



Experiments to test this possibility are in progress.

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