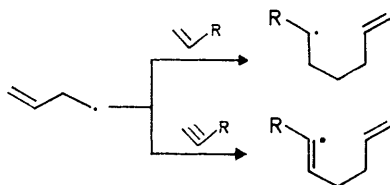


Novel Method of producing Radicals of the Hex-5-enyl Type

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Addition to alk-1-enes or alk-1-yne of the radical obtained from 3,3,4,4-tetrafluoro-4-iodobut-1-ene by either peroxide or metal-salt initiation, provides a convenient route to hex-5-enyl radicals. The size of the rings produced from these radicals is discussed on the basis of the polarisation of the terminal double bond and of the nature of the attacking radical.

WHEN a free-radical centre is generated at the position δ to a double bond, cyclisation occurs very readily. Julia has studied and reviewed the cyclisation reactions.¹ Unsaturated radicals of the hex-5-enyl type have been obtained¹ by decarbonylation of aldehydes, decomposition of alkyl peroxides, electrolysis of acids, treatment of acids with lead tetra-acetate, and reduction of alkyl and arylhalides with organotin hydrides. All these reactions generate the unpaired electron on a carbon which is δ to a double bond. We hoped to obtain the same result by adding β -alkenyl radicals to α -olefins and acetylenes.



This route appeared to be a suitable method for the study of new radicals from commercially available monomers. An early example of this route is the

¹ M. Julia, *Rec. Chem. Progr.*, 1964, **25**, 3; *Pure Appl. Chem.*, 1965, **15**, 167; *Accounts Chem. Res.*, 1971, **4**, 386.

ready dimerisation² of 3,3,4,4-tetrafluoro-4-iodobut-1-ene (I). Addition of the radical (II) to a multiple bond yields a hex-5-enyl type radical which can rearrange to its cyclic isomers. The limiting factor could be the relative rate of the addition of (II) to the unsaturated substrate with respect to the dimerisation rate of olefin (I). In fact, the rate pattern found for the additions of (II) reflects general principles that govern radical additions, and parallels that found for CF_3 radicals.

Free-radical reaction of compound (I) with alkenes (IV)—(VIII) or alkynes (IX) and (X) occurred readily at 120° when Bu^t_2O_2 was used as initiator. In order to minimise polymerisation of the olefins (IV)—(VI), we used an excess of compound (I). In the reaction with styrene the initiation was of the 'redox-transfer' type³ and therefore the use of an excess of (I) was unnecessary, since chain-transfer occurs with iron(III) ions. However, in the same reaction we observed the anticipated³ interaction of styrene with the initiator, and the volatile fraction contained 1,3-diphenylbut-1-ene and 4-iodo-1,3-diphenylbut-1-ene. Reactions took place in sealed ampoules, and with the olefin (VII) in an autoclave. Table I shows some typical experiments. The reaction

² P. Piccardi and M. Modena, *Chem. Comm.*, 1971, 1041.

³ M. Asscher and D. Vofsi, *J. Chem. Soc.*, 1963, 3921.

product contained 1:1 adducts (XI)—(XXII) and higher telomers, and only the former were investigated. In the reaction of (I) with the olefin (VI), beside the product of ring closure (XIV), a γ -lactone (XV) was detected. The presence of ethyl iodide in the reaction products has been taken as an indication that lactone

merisation might preferentially remove one of the cyclised radicals, thus affecting the ratio of the five-membered to six-membered ring isomer. If, as seems probable, this factor does not alter substantially the results in Table 3, it is surprising that species with the radical centre α to a carboxylate, or a cyano-group

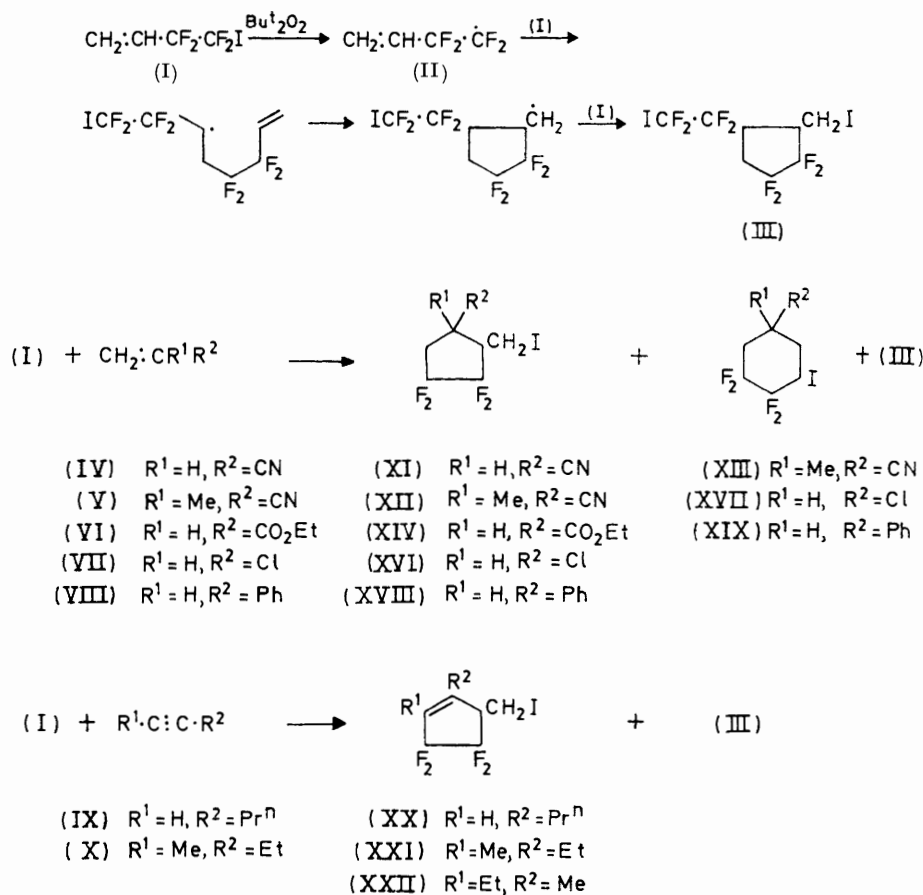


TABLE I
Experimental results

(I) (g)	Alkene or alkyne (g)	Molar ratio	Bu ^t ₂ O ₂ (g)	Volatile products		Residue (g)	Yields (%) of volatile products ^b
				B.p./°C at <i>p</i> /mmHg	Yield (g)		
28.8	(IV) 2	3:1	0.3	80—90 at 0.6	2.6	2.6	(IXa) (15.4), (XIb) (13.6), (IIIa) (35.5), (IIIb) (35.5)
28.8	(V) 2	3:1	0.3	75 at 0.6	2.7	2.7	(XIIa) (20), (XIIb) (30), (IIIa) (22), (IIIb) (22), (XIII) ^c (6)
28.8	(VI) 3.8	3:1	0.3	69—73 at 0.3	6.2	6.2	(XV) (7), (XIVa) (19), (IIIa) (32), (IIIb) (32), (XIVb) (10)
10.5	(IX) 2.8	1:1	0.1	80—98 at 10	3.0	1.5	(XX) (80), (IIIa) (10), (IIIb) (10)
10.5	(X) 2.8	1:1	0.1	80—98 at 10	2.8	1.5	(XXI) (36), (XXII) (36), (IIIa) (14), (IIIb) (14)
100	(VII) 13	1.9:1	1.0	45—65 at 0.2	31	27	(XVIa) (22), (XVII) ^d (5), (XVIb) (31), (XVII) ^d (2), (IIIa) (20), (IIIb) (20)

^a Molar ratio (I) : alkene or alkyne. ^b Analysed by g.l.c.: products are listed in order of elution (a = *cis*-, b = *trans*-isomer). ^c The product is a mixture of stereoisomers. ^d *cis*- or *trans*-isomer.

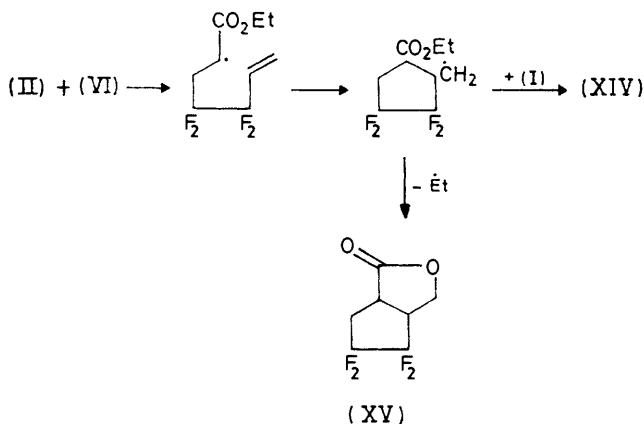
formation occurs through elimination of an ethyl radical. A similar cyclisation has recently been reported.⁴

Table 2 shows the composition of the mixtures of isomers obtained during the cyclisation. The results may be affected by the formation of telomers: telo-

should close to give a cyclopentane derivative with a higher degree of specificity than species with the radical centre α to a chlorine atom. This situation can possibly be rationalised in terms of the greater electrophilic character of $-\text{CH}_2\cdot\dot{\text{C}}\text{H}\cdot\text{CN}$ or $-\text{CH}_2\cdot\dot{\text{C}}\text{H}\cdot\text{CO}_2\text{Et}$ radicals

⁴ Y. Rori and J. Tsuji, *Tetrahedron*, 1972, **28**, 29.

than of $-\text{CH}_2\dot{\text{C}}\text{HCl}$; this would make the relatively electron-rich δ end $-\text{CF}_2\text{CH}=\text{}$ of the terminal double bond more selective in reactions with the more electrophilic



radicals. Therefore it appears that there are important factors which influence the course of these cyclisations in addition to those implied in other cases, *e.g.*, in non-fluorinated olefins. Further experiments might show

TABLE 2

Proportion of five- and six-membered ring products

		Cyclopentane derivatives (%)	Cyclohexane derivatives (%)
R ¹	R ²		
H	CF ₂ CF ₂ I	100	
H	CN	100	
Me	CN	90	10
H	CO ₂ Et	100	
H	Cl	88.5	11.5
H	Ph	76	24

		Cyclopentane derivatives (%)	Cyclohexane derivatives (%)
R ¹	R ²		
H	Pr ⁿ	100	
Me	Et	100	
Et	Me	100	

whether the foregoing significant dependence of the direction of intramolecular addition on the polarisation of both the double bond and the attacking radical is a general phenomenon.

EXPERIMENTAL

Techniques.—Products were identified by elemental analysis, ¹H and ¹⁹F n.m.r. spectroscopy [Varian HA100 instrument; the ¹⁹F figures quoted are chemical shifts in p.p.m. from internal trichlorofluoromethane and ¹H figures are τ values (internal tetramethylsilane standard)], and mass spectrometry (Hitachi-Perkin-Elmer RMU/6E instru-

ment). Analytical g.l.c. was carried out with a column (2.5 m \times 4 mm) packed (20%) with high vacuum silicone grease on Chromosorb or a column (6 m \times 4 mm) packed (20%) with Carbox 20M on Chromosorb; temperatures were 80–200 °C (2.5° min⁻¹).

General Procedure for the Reactions of 3,3,4,4-Tetrafluoro-4-iodobut-1-ene (I) with Alkenes and Alkynes.—The reactions of compound (I) with alkenes (IV)–(VI) and alkynes (IX) and (X) were carried out in 28 ml ampoules by agitating at 130 °C for 5 h. The reagents (see Table I for the appropriate amounts) were charged as follows. The ampoule, containing a weighed amount of Bu^t₂O₂, was evacuated and cooled to –50 °C. The appropriate mixture of compound (I) and the alkene or alkyne was injected into the ampoule, which was then sealed and placed in the thermostatted bath. After the reaction the ampoule was broken and the contents distilled. The volatile fraction was analysed by g.l.c. and the products separated by semi-preparative g.l.c. The reaction of compound (I) with vinyl chloride (VII) was carried out in an 'Hastelloy' rocking autoclave (200 ml) at 130 °C for 5 h. Reaction of compound (I) with styrene is described below.

Identification of Products.—4-Cyano-1,1,2,2-tetrafluoro-3-iodomethylcyclopentane (XI) (Found: C, 28.0; H, 2.0; N, 4.6. C₇H₆F₄IN requires C, 27.4; H, 2.0; N, 4.5%); τ (CCl₄) (isomeric mixture) 6.6 (2H, complex, CH₂I), 6.8–7.6br (4H, CH₂CHCH); ϕ^* (*cis*-isomer) ⁶ 114.0 and 120.5 (2F, AB, *J* 244 Hz, CH₂CF₂) and 119.0 and 130.0 (2F, AB, *J* 242 Hz, CF₂CH); ϕ^* (*trans*-isomer) ⁶ 107.4 and 119.8 (2F, AB, *J* 242 Hz, CF₂CH) and 125.8 and 129.8 (2F, AB, *J* 240 Hz, CH₂CF₂); *m/e* 307 (*M*⁺, 100%), 180 (*M*⁺ – I, 35), 160 (*M* – HF – I, 39), 153 (*M* – I – HCN, 9.5), 133 (*M* – HF – I – HCN, 25), 116 (*M* – I – C₂H₂F₂, 93), and 77 (C₃H₃F₂⁺, 33).

4-Cyano-1,1,2,2-tetrafluoro-3-iodomethyl-4-methylcyclopentane (XII) (Found: C, 30.5; H, 2.5; N, 4.4. C₈H₈F₄IN requires C, 29.95; H, 2.5; N, 4.35%); τ (CCl₄) (*cis*-isomer) ⁵ 6.5 and 6.7 (2H, AB part of an ABX system, *J*_{AX} 6.3, *J*_{BX} 8.3, *J*_{AB} 11.4 Hz, CH₂I), 7.1 (1H, complex, CHCH₂I), 7.35–7.9 (2H, complex, CH₂), and 8.26 (3H, s, CH₃); ϕ^* 122.3 and 128.2 (2F, AB, *J* 241 Hz, CH₂CF₂) and 110.4 and 122.6 (2F, AB, *J* 244 Hz, CF₂CH); τ (CCl₄) (*trans*-isomer) ⁵ 6.52–7.0 (2H, complex, CH₂I), 7.2 (1H, complex, CHCH₂I), 7.34–7.9 (2H, complex, CH₂), and 8.5 (3H, s, Me); ϕ^* 119.7 and 123.8 (2F, AB, *J* 244 Hz, CH₂CF₂) and 108.2 and 118.2 (2F, AB, *J* 244 Hz, CF₂CH); *m/e* (isomeric mixture) 321 (*M*⁺, 100%), 194 (*M* – I, 18), 174 (*M* – HF – I, 28), 167 (*M* – I – HCN, 18), 147 (*M* – HF – I – HCN, 22), and 77 (C₃H₃F₂⁺, 62).

5-Cyano-1,1,2,2-tetrafluoro-3-iodo-5-methylcyclohexane (XIII), *m/e* (isomeric mixture) 321 (*M*⁺, 100%), 194 (*M* – I, 20), 174 (*M* – HF – I, 37), 167 (*M* – I – HCN, 16), 147 (*M* – HF – I – HCN, 37), and 77 (C₃H₃F₂⁺, 85).

Ethyl 3,3,4,4-tetrafluoro-2-iodomethylcyclopentanecarboxylate (XIV) (Found: C, 31.0; H, 3.0. C₉H₁₁F₄IO₂ requires C, 30.55; H, 3.15%); τ (CCl₄) (isomeric mixtures) 5.8 (2H, q, *J* 7 Hz, OCH₂CH₃), 6.7 (2H, complex, CH₂I), and 6.8–7.9br (4H, CH₂CHCH); ϕ^* (*cis*-isomer) ⁶ 117.5 and 130.1 (2F, AB, *J* 241 Hz, CF₂CH) and 113.8 and 120.1 (2F, AB, *J* 242 Hz, CF₂CH₂); *m/e* 354 (*M*⁺, 4.5%), 309 (*M* – C₂H₅O, 13.5), 261 (*M* – C₃H₅O₂ – HF, 8), 227 (*M* – I, 75), 199 (*M* – I – C₂H₄, 44), 77 (C₃H₃F₂⁺, 37), and 29 (C₂H₅⁺, 100).

⁵ A. L. Henne and S. Kaye, *J. Amer. Chem. Soc.*, 1950, **72**, 3369.

⁶ P. Piccardi, M. Modena, and L. Cavalli, *J. Chem. Soc. (C)*, 1971, 3959.

3,3,4,4-Tetrafluoro-2-hydroxymethylcyclopentanecarboxylic acid γ -lactone (XV) (Found: C, 42.5; H, 3.1. $C_7H_6F_4O_2$ requires C, 42.45; H, 3.05%), m.p. 45 °C; τ (CCl_4) (isomerically pure) 5.5 (2H, complex, CH_2O), 6.75 (2H, complex, CHCH), and 7.5 (2H, complex, CH_2CF_2); ϕ^* 121.3 and 138.6 (2F, AB, J 247 Hz, CF_2CH) and 126.5 and 129.1 (2F, AB, J 246 Hz, CF_2CH_2); m/e 198 (M^+ , 1.1%), 154 ($M - CO_2$, 47), 140 ($M - C_2H_2O_2$, 17), 139 ($M - CO_2 - CH_3$, 30), 90 ($M - CO_2 - C_2H_2F_2$, 90), 85 ($M - CO_2 - CF_3$, 100), and 77 ($C_3H_3F_2^+$, 39).

4-Chloro-1,1,2,2-tetrafluoro-3-iodomethylcyclopentane (XVI) (Found: C, 22.9; H, 2.0. $C_6H_6ClF_4I$ requires C, 22.75; H, 1.9%), τ (CCl_4) (*cis*-isomer) δ 6.05 (1H, dd, J 8 and 7 Hz, CHCl), 6.69 (2H, d, J 8 Hz, CH_2I), and 6.9–7.7 (3H, complex, $CF_2CH_2 + CHCH_2I$); ϕ^* 116.3 and 129.2 (2F, AB, J 241 Hz, CF_2CH) and 111 and 118.9 (2F, AB, J 244 Hz, CF_2CH_2); τ (CCl_4) (*trans*-isomer) δ 5.42 (1H, complex, CHCl), 6.64 (2H, complex, CH_2I), and 7.0–7.3 (3H, complex, $CF_2CH_2 + CHCH_2I$); ϕ^* 104.3 and 113.6 (2F, AB, J 244 Hz, CF_2CH) and 119.4 and 121.7 (2F, AB, J 241 Hz, CF_2CH_2); m/e (isomeric mixture) 318/316 (M^+ , 23/70.3%), 191/189 ($M - I$, 10.8/33.1), 171/169 ($M - HF - I$, 23.4/72.1), 153 ($M - HCl - I$, 100), and 133 ($M - HF - I - HCl$, 67).

5-Chloro-1,1,2,2-tetrafluoro-3-iodocyclohexane (XVII), τ (CCl_4) 5.4 (1H, complex, CHCl), 5.78 (1H, complex, CHI), and 7.3–7.6 (4H, complex, $CH_2CHClCH_2$); m/e (isomeric mixture) 318/316 (M^+ , 20/59%), 191/189 ($M - I$, 2.5/2.3), 171/169 ($M - HF - I$, 5.1/15.8), 153 ($M - I - HCl$, 100), and 133 ($M - HF - I - HCl$, 41).

3,3,4,4-Tetrafluoro-5-iodomethyl-1-propylcyclopentane (XX) (Found: C, 33.65; H, 3.45. $C_9H_{11}F_4I$ requires C, 33.55; H, 3.45%); τ (CCl_4) 4.28br (1H, CH_2C), 6.79 (3H, complex, $CHCH_2I$), 7.84 (2H, m, $CH_2C:C$), 8.45 (2H, sextet, J 7 Hz, CH_2CH_3), and 9.06 (3H, t, J 7 Hz, CH_3); ϕ^* 113.8 and 127.4 (2F, AB, J 240 Hz, CF_2CH) and 107.2 and 111.7 (2F, AB, J 258 Hz, CF_2CH_2); m/e 322 (M^+ , 20%), 195 ($M - I$, 60), 153 ($M - I - C_3H_6$, 100), and 77 ($C_3H_3F_2^+$, 33).

1-Ethyl-3,3,4,4-tetrafluoro-5-iodomethyl-2-methylcyclopentane (XXI) (Found: C, 33.6; H, 3.4. $C_9H_{11}F_4I$ requires C, 33.55; H, 3.45%); τ (CCl_4) 6.82 (2H, complex, CH_2I), 7.75 (3H, complex, $CH_2C:C + CHCH_2I$), 8.14 (3H, t, J 7 Hz, $CH_3C:C$), and 8.9 (3H, t, J 8 Hz, CH_2CH_3); ϕ^* 114 and 128 (2F, AB, J 240 Hz, CF_2CH) and 100 and 115.8

(2F, AB, J 258 Hz, $CF_2C:C$); m/e 322 (M^+ , 20%), 195 ($M - I$, 100), 175 ($M - HF - I$, 9), and 77 ($C_3H_3F_2^+$, 25).

2-Ethyl-3,3,4,4-tetrafluoro-5-iodomethyl-1-methylcyclopentane (XXII) (Found: C, 33.6; H, 3.6. $C_9H_{11}F_4I$ requires C, 33.55; H, 3.45%); τ (CCl_4) 6.82 (2H, complex, CH_2I), 7.75 (3H, complex, $CH_2C:C + CHCH_2I$), 8.24 (3H, s, $CH_3C:C$), and 8.93 (3H, t, J 7 Hz, CH_2CH_3); ϕ^* 114 and 128 (2F, AB, J 260 Hz, CF_2CH) and 111.8 and 118.5 (2F, AB, J 255 Hz, $CF_2C:C$); the mass spectrum was similar to that of the isomer (XXI).

Reaction of 3,3,4,4-Tetrafluoro-4-iodobut-1-ene (I) with Styrene.—Compound (I) (4.2 g, 16.9 mmol), styrene (1.7 g, 16.8 mmol), acetonitrile (1.38 g, 33.8 mmol), n-butylamine (0.0185 g), and $FeCl_2 \cdot 4H_2O$ (0.0278 g) were sealed in a Pyrex tube and heated in an oil-bath at 130 °C for 7 h while stirring. n-Pentadecane (internal reference) was added to the cooled mixture which was analysed and separated by g.l.c. The recovered products (1.25 g) (in order of elution) had the following molar composition: *cis*-(III) 0.73%, *trans*-(III) 0.78, *cis*- and *trans*-1,1,2,2-tetrafluoro-3-iodomethyl-4-phenylcyclopentane (XVIII) 26.8, *cis*- and *trans*-1,1,2,2-tetrafluoro-3-iodo-5-phenylcyclohexane (XIX) 5.4 and 1.2, 'distyrene' δ 57.6, and a product 7.5 [m/e 334 (M^+ , 20.3%), 193 ($M - CH_2I$, 79.5), 115 ($M - CH_2I - C_6H_6$, 100), 91 ($C_7H_7^+$, 66.5), and 77 ($C_6H_5^+$, 17); presumably 4-iodo-1,3-diphenylbut-1-ene.]

Identification of Products.—1,1,2,2-Tetrafluoro-3-iodomethyl-4-phenylcyclopentane (XVIII) (Found: C, 40.4; H, 3.1. $C_{12}H_{11}F_4I$ requires C, 40.25; H, 3.1%); τ (CCl_4) (isomeric mixture) 2.76 (5H, complex, Ar) and 6.3–7.8br (6H, CH_2I and ring protons); ϕ^* (*cis*-isomer) δ 115.8 and 131.2 (2F, AB, J 239 Hz, CF_2CH) and 110.6 and 119.8 (2F, AB, J 240 Hz, CF_2CH_2); ϕ^* (*trans*-isomer) δ 111.6 and 123.0 (2F, AB, J 240 Hz, CF_2CH) and 125.3 (2F, complex, CF_2CH_2); m/e 358 (M^+ , 94.5%), 231 ($M - I$, 100), 211 ($M - HF - I$, 43), 153 ($M - I - C_6H_6$, 15), 91 ($C_7H_7^+$, 80), and 77 ($C_3H_3F_2^+$ and $C_6H_5^+$, 69). 1,1,2,2-Tetrafluoro-3-iodo-5-phenylcyclohexane (XIX) (isomeric mixture); 1H n.m.r. spectrum showed the resonance of the CHI group at τ 5.8; m/e 358 (M^+ , 40%), 231 ($M - I$, 45), 211 ($M - HF - I$, 23), 153 ($M - I - C_6H_6$, 100), 133 ($M - HF - I - C_6H_6$, 24), 91 ($C_7H_7^+$, 48), and 77 ($C_3H_3F_2^+$ and $C_6H_5^+$, 36).

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