CONCLUSIONS

1. The applicability of the electrolysis of CF_3COOH in the presence of fluoroolefins for the preparative synthesis of several fluorohydrocarbons is shown.

2. The orientation of the attack of fluoroolefins by $\dot{C}F_3$ radicals, generated under conditions of anodic oxidation of trifluoroacetate ions, matches that which is observed under conditions of thermal or photochemical generation.

3. Under conditions of anodic generation of $\dot{C}F_3$ radicals, evidently, strong absorption of them does not occur on the surface of the electrode.

LITERATURE CITED

1. V. A. Grinberg, V. R. Polishchuk, E. I. Mysov, V. V. Tsodikov, L. S. German, L. S. Kanevskii, and Yu. B. Vasil'ev, Izv. Akad. Nauk SSSR, Ser. Khim., 2875 (1977).
2. Pat. FRG 937919, (1956); Chem. Abstr., 53, 3950 (1959).
3. H. C. Low, J. M. Tedder, and J. C. Walton, J. Chem. Soc. Faraday Trans. 1, 72, 1300 (1976).
4. G. L. Fleming, R. N. Haszeldine, and A. E. Tipping, J. Chem. Soc. Perkin Trans. 1, 574 (1973).
5. J. N. Cape, A. G. Greig, J. M. Tedder, and J. C. Walton, J. Chem. Soc. Faraday Trans. 1, 71, 592 (1975).
6. P. Camilleri, R. M. Marshall, and H. Purnell, J. Chem. Soc. Faraday Trans. 1, 71, 1491 (1975).
7. V. A. Grinberg, V. R. Polishchuk, L. S. Kanevskii, L. S. German, Yu. B. Vasil'ev, Izv. Akad. Nauk SSSR, Ser. Khim., 673 (1978).
8. G. E. Hawkes, J. H. P. Utley, G. B. Yates, J. Chem. Soc. Perkin Trans. 2, 1709 (1976).
9. G. V. D. Tiers, J. Amer. Chem. Soc. 78, 2914 (1956).
10. R. D. Dresdner, F. N. Tlumac, and J. A. Young, J. Am. Chem. Soc., 82, 5831 (1960).

1,4 ADDITION TO A PERFLUORINATED CROSS-CONJUGATED TRIENE

E. G. Ter-Gabriélyan, N. P. Gambaryan,
É. P. Lur'e, and P. V. Petrovskii

UDC 542.955:547.316.6'161

We have previously shown that perfluoroisobutylene is converted to triene (I) by the action of Ph_3P [1]; triene (I) is a representative of a class of perfluoropolyenes which has hardly been studied. Formally, triene (I) is the first perfluorinated system with cross conjugation (see the work of Phelan and Orchin [2]); however, construction of Stewart models shows that one of the heptafluoroisobutenyl groups in this molecule is formed almost completely out of the plane of conjugation. Thus, triene (I) may be considered as a conjugated diene with an unsaturated substituent. The accumulation of trifluoromethyl groups leads to electron depletion of the double bonds in (I), which results in its inertness even towards such a powerful electrophile as SO_3. In contrast to perfluorobutylene [3], (I) does not react with SO_3 upon prolonged heating up to 100°C. On the other hand, in reactions with nucleophilic reagents, (I) is more active than perfluoro-1,3-dienes which yield products of 1,2 addition with alcohols in the presence of Et_3N and with water [4, 5] and products of vinyl substitution with amines [6]. Only the cyclic dimer of perfluorodimethylallene with two exocyclic double bonds adds water in the 1,4 position [7]. Triene (I) reacts with alcohol, water, and aniline under mild conditions without a catalyst and yields products of 1,4 addition.* The nucleophilic species adds only at position 1 apparently due to the special stability of the intermediate carbanion (III)

---

*The vigorous reaction of (I) with NH_3 is accompanied by the mineralization of most of the fluorine atoms. Triene (I) reacts with CH_2N_2 at the 1,2 bond with the formation of a cyclopropane likely due to the great stability of the intermediate (3 + 2) than that for the (3 + 4) cycloadduct.

Institute of Heteroorganic Compounds, Academy of Science of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1061-1064, May, 1979. Original article submitted December 20, 1977.

TABLE 1. ^{13}C NMR Spectral Parameters of Compounds (IIb) and (IV)

Parameters	CF_3	C^1	C^2	C^{3*}	C^4	C^{5*}	C^6	Me
Ether (IIb), δ, ppm	~120†	81,76 h	112,53 dd	156,49 dd	51,22 ddh	158,70 dd	113,70 dh	55,05 q††
J, Hz	280	29,4	22,6; 18,3	290,3; 5,5	133,0; 24,6; 32,6**	284,8; 12,9	22,3; 32,6**	148,0
Allene(V), δ, ppm	~120‡	80,47 h	103,37 d	206,06 s	~120	157,40 d	112 dh	55,35 q††
J, Hz	276‡	29,4	25,0	—	—	291,4	14,7; 33,8**	148,5

---

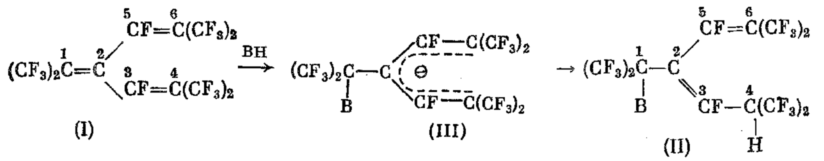
*Tentative signal assignment.

†Group of quartets.

‡$CF_3C(1)$ 120.95 q, J = 291.2 Hz.

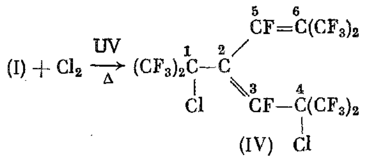
**$J_{^{13}C-CF_3}$.

††$^{13}C-\{^1H\}$ singlet.



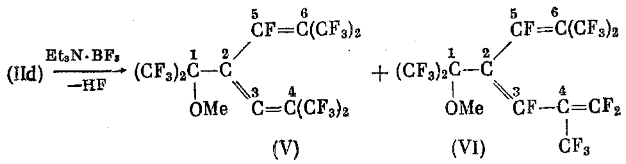
B=HO (a), MeO (b), EtO (c), PhNH (d)

This order of addition is also contained for radical reactions; triene (I) does not react with bromine but is chlorinated upon irradiation with the formation of 1,4 adduct (IV)



The structure of the products of 1,4 addition is supported both by the spectral characteristics (Tables 1 and 2) and chemical analysis. A characteristic signal, namely, a doublet of heptets for the proton of the $(CF_3)_2CHCF$ group, is found in the PMR spectra of all the addition products (II). In the ^{13}C NMR spectrum of (IIb), the carbon atoms of the $C(3)F=C(2)-C(5)F$ group are seen as three doublets. In the IR spectrum of the addition products (II), two bands are observed at 1670-1675 and 1700-1710 cm^{-1}.

Allene (V) with a trace of triene (VI) is formed upon the dehydrofluorination of diene (IIb) with finely ground KOH or the $Et_3N \cdot BF_3$ adduct (see our previous work [8])



A band in the vicinity of 2000 cm^{-1} is observed in the IR spectrum of allene (V), while the carbon atoms of the $C^{(3)}=C^{(2)}-C(5)F$ group are seen in the ^{13}C NMR spectrum as a singlet and two doublets.

Only triene (VII) is formed in the dehydrofluorination of the diene (IId) possibly as a consequence of intramolecular hydrogen bonding both in starting (IId) and in the product (VII) (the 3460 cm^{-1} band for NH. . . F in the IR spectrum)

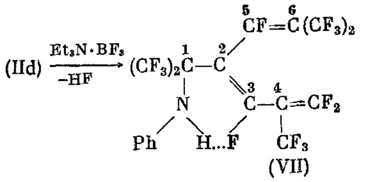


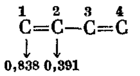
TABLE 2. ^{19}F NMR Spectral Parameters (δ, ppm) of Compounds (IIa)-(IId) and (IV)

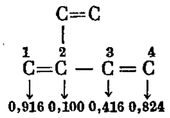
Compound	$(CF_3)_2C(1)$ m	$(CF_3)_2C(4)$ m	$(CF_3)_2C(6)$ m	FC(3) m	FC(5) m
(IIa)	−3,0; −0,4	−13,1; −11,6	−16,5	+8,7	−13,0
(IIb)	−7,1 * ddq; −5,8	−13,2; −11,3	−16,5	+6,6	−14,7
(IIc)	−7,1 * ddq; −5,8	−13,3; −11,3	−16,5	+7,6	−14,7
(IId) (in CCl_4)	−8,4 * ddq; −6,3	−14,2; −11,8	−17,0	+0,5	−14,0
(IV)	−10,3; −6,6	−7,8 br.s	−16,3	−10,5	−17,8

---

*$J_{CF_3\text{-}CF} = J_{CF_3\text{-}CF_3}$ = 11.3 (IIb, c); 11.9 Hz (IId).

Thus, triene (I) both in activity and addition regioselectivity differs sharply from perfluoro-1,3-dienes. Therefore, despite significant steric hindrance leading to loss of planarity and the electron-withdrawing effect of the CF_3 groups, features of electron structure characteristic for systems with cross conjugation are retained in (I), specifically, the special reactivity of position I and the tendency towards 1,4 addition. These features of cross-conjugated systems are evident from a comparison of the molecular diagrams for 1,3-butadiene and 2-methylene-1,4-pentadiene [9]





The free valence index in the cross-conjugated triene is enhanced for C(1) and diminished for C(2).

EXPERIMENTAL

The NMR spectra were taken on Perkin–Elmer R-12 (^1H, 60 MHz), Perkin–Elmer R-20 (^{19}F, 60 MHz), Perkin–Elmer R-32 (^{19}F, 84.6 MHz; ^1H, 90 MHz), Bruker HX-90 (^{13}C, 22.635 MHz), and Bruker WH-180 (^{13}C, 45.28 MHz) spectrometers. The chemical shifts in ppm are given relative to external standards HMDS (^1H, δ scale), CF_3CO_2H (^{19}F), and CS_2 (^{13}C, δ 192.8). The IR spectra, were taken on a UR-20 spectrometer. Preparative GLC was performed on a Carlo–Erba chromatography with a column packed with QF-1 and helium gas carrier.

Reaction of Triene (I) with Nucleophiles. a) A mixture of 8.6 g (I), 15 ml acetone, and 1 ml water was stirred at ~20°C for 24 h until it became homogeneous. Water was added, and the lower layer was separated and dried with magnesium sulfate. Pure (IIa) was obtained from the fraction with bp 157-160°C (3.1 g) which contained 80% alcohol (IIa) by preparative GLC. Found: C 26.58; H 0.00; F 70.59%. Calculated for $C_{12}H_2F_{20}O$: C 26.57; H 0.37; F 70.11%. IR spectrum (ν, cm^{-1}): 1670 (C=C), 1710 (C=C). PMR spectrum (ν, ppm): 3.3 s (OH), 3.9 d. h $(CF_3)_2CHCF$, J_{H-F} = 24.5, and J_{H-CF_3} = 6.6 Hz.

b) A mixture of 22.2 g (I) in 10 ml abs. methanol was heated at reflux for 24 until it became homogeneous. Water was added and the lower layer was separated, washed with aq. $CaCl_2$, water, and dried with $CaCl_2$. A yield of 17.4 g (73.8%) ether (IIb) (bp 160-164°C) was obtained by distillation. Found: C 28.13; H 0.66%. Calculated for $C_{13}H_4F_{20}O$: C 28.06; H 0.72%. IR spectrum (ν, cm^{-1}): 1675 (C=C), 1705 (C=C). PMR spectrum: 3.6 s (MeO), 3.9 d. h $(CF_3)_2CHCF$, J_{H-F} = 26.7, J_{H-CF_3} = 6.7 Hz.

c) A mixture of 3.7 g (I) and 6.4 g abs. ethanol was maintained for 10 days at ~20°C until it became homogeneous. The reaction solution was treated as in run b. Distillation yielded 2.9 (65.8%) ether (IIc) (bp 165-169°C). Found: C 29.19; H 1.19%. Calculated for $C_{14}H_6F_{20}O$: C 29.47; H 1.05%. IR spectrum (ν, cm^{-1}): 1675 (C=C), 1705 (C=C). PMR spectrum: 1.1 t (Me), 3.7 q (CH_2, $J_{CH_3-CH_2}$ = 6.7 Hz), 3.7 d. h $(CF_3)_2CHCF$, J_{H-F} = 35.8, J_{H-CF_3} = 6.7 Hz.

d) To 4.7 g (I) in 5 ml abs. ether, 0.85 g aniline in 3 ml abs. ether was added with stirring and ice cooling. The mixture was maintained for 20 h at ~20°C. Distillation yielded 4.3 g (93%) pure (IId) with bp 56-60°C (0.01 mm Hg). Found: C 35.29; H 1.08%; F 61.32; N 2.48%. Calculated for $C_{18}H_7F_{20}N$: C 35.01; H 1.13; F 61.50; N 2.26%. IR spectrum (ν, cm^{-1}): 1660 (C=C), 1690 (C=C), 3460 (NH. . . F). PMR spectrum (in CCl_4, δ, ppm): 3.7 s (NH), 4.5 d. h $(CF_3)_2CHCF$, J_{H-F} = 26.0, and J_{H-CF_3} = 6.7 Hz.

Reaction of Triene (I) with Chlorine. An excess of chlorine was bubbled into 2.6 g (I) for 3 h with UV irradiation. Distillation yielded 2 g (68%) pure (IV) with bp 102-104°C (60 mm Hg). Found: C 23.71; F 63.89; Cl 12.48%. Calculated for $C_{12}F_{20}Cl_2$: C 24.20; F 63.87; Cl 11.93%. IR spectrum (ν, cm^{-1}): 1650 (C=C), 1700 (C=C).

Dehydrofluorination of Ether (IIb). To 2.5 g ether (IIb) in 5 ml abs. ether, 0.9 g $Et_3N \cdot BF_3$ in 2 ml abs ether was added with stirring. The precipitate was filtered off after 15 h. Distillation of the filtrate yielded 1.65 g (58%) of a mixture with bp 33-35°C (3 mm Hg), which according to GLC consisted of 98% allene (V) and 2% triene (VI). Found: C 29.14; H 0.83; F 66.84%. Calculated for $C_{13}H_3F_{19}O$: C 29.10; H 0.56; F 67.35%. Pure (V) was isolated by preparative GLC. IR spectrum (ν, cm^{-1}): 2000 (C=C=C), 1690 (C=C). PMR spectrum (δ, ppm): 3.5 s (MeO). ^{19}F NMR spectrum: −18.0 m [3F, $CF_3C(6)$], −17.0 d. q [3F, $CF_3C(6)$], $J_{CF_3-F} = 22.4$, $J_{CF_3-CF_3} = 8.7$ Hz, −16.0 br. s [(6F, $(CF_3)_2C(4)$], −6.3 m [6F, $(CF_3)_2C(1)$], −5.0 m [1F, FC(5)]. Pure (VI). IR spectrum (in CCl_4, ν, cm^{-1}): 1660 (C=C), 1690 (C=C), 1730 ($C=CF_2$). PMR spectrum (δ, ppm): 3.5 s (MeO). ^{19}F NMR spectrum: −18.0 m [6F, $(CF_3)_2C(6)$], −19.7 m [3F, $CF_3C(4)$], −15.2 m [2F, $CF_2C(4)$], −12.6 m [1F, FC(3)*], −9.2 m [1F, FC(5)*], −8.3 d. d. q [3F, $CF_3Cl(1)$, $J_{CF_3-F} = J_{CF_3-CF_3} = 8.7$ Hz], −6.6 m [3F, $CF_3C(1)$].

Dehydrofluorination of Butene (IId). To 4.3 g (IId) in 5 ml abs. ether, 1.2 g $Et_3N \cdot BF_3$ in 5 ml abs. ether was added with stirring and ice cooling. The reaction mixture was maintained for 25 h at ~20°C and the precipitate was filtered off. Distillation of the filtrate yielded 2.8 g (68%) pure triene (VII) with bp 59-63°C (0.01 mm). Found: C 49.75; H 2.30; F 42.03; N 5.98%. Calculated for $C_{18}H_6F_{19}N$: C 49.79; H 2.35; F 42.04; N 5.81%. IR spectrum (ν, cm^{-1}): 1660 (C=C), 1690 (C=C), 1730 (C=C). PMR spectrum (δ, ppm): 3.9 s (NH), 6.7 m (Ph). ^{19}F NMR spectrum: −18.4 m [3F, $CF_3C(6)$], −16.0 m [6F, $CF_3C(4)$; $CF_3C(6)$], −14.5 m [3F, $CF_2C(4)$ and FC(3)*], −10.5 m [1F, FC(5)*], −8.4 d.d.q [3F, $CF_3C(1)$, $J_{CF_3-F} = J_{CF_3-CF_3} = 11.9$ Hz], −4.2 m [3F, $CF_3C(1)$].

CONCLUSIONS

Perfluoro-(2-isobutenyl-1,1,4,4-tetramethyl-1,3-butadiene) yields 1,4 addition products both in nucleophilic addition and in radical chlorination.

LITERATURE CITED

1. I. L. Knunyants, E. G. Ter-Gabriélyan, Yu. V. Zeifman, Z. V. Safronova, N. P. Gambaryan, E. I. Mysov, A. I. Lutsenko, and P. V. Petrovskii, Dokl. Akad. Nauk SSSR, 228, 1344 (1976).
2. X. F. Phelan and M. Orchin, J. Chem. Educ., 45, 633 (1968).
3. N. B. Kaz'mina, I. L. Knunyants, G. M. Kuz'yants, E. I. Mysov, and É. P. Lur'e, Izv. Akad. Nauk SSSR, Ser. Khim., 118 (1979).
4. I. L. Knunyants, B. L. Dyatkin, and E. P. Mochalina, Izv. Akad. Nauk SSSR, Ser. Khim., 1483 (1962).
5. N. B. Kaz'mina, G. S. Krasnikova, É. P. Lur'e, E. I. Mysov, and I. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim., 2525 (1975).
6. I. L. Knunyants, B. L. Dyatkin, and L. S. German, Dokl. Akad. Nauk SSSR, 124, 1065 (1959).
7. P. W. L. Bosbury, R. Fields, R. N. Haszeldine, and D. Morun, J. Chem. Soc., Perkin Trans. 1, 1173 (1976).
8. L. A. Rozof, Yu. V. Zeifman, N. P. Gambaryan, Yu. A. Cheburkov, and I. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim., 2750 (1976).
9. C. A. Coulson and R. Daudel, Dictionnaire des grandeurs theoriques III, Paris (1955).

---

*Tentative assignment of signals.