6-MTN on Raney Ni at 60°C. The latter could not be isolated in pure form from the oxidation products since under the distillation conditions it is completely dehydrated to 6-MDN. Found: 82.2% C; 7.61% H. C₁₁H₁₂O. Calculated: 82.46% C; 7.55% H.

CONCLUSIONS

1. The primary oxidation products of 6-methoxytetralin in the presence of polydehydrobutoxychrysoidine are the hydroperoxides of 6- and 7-methoxytetralin.

2. The conditions for the maximum yield of 6-methoxytetralone are found.

LITERATURE CITED

- 1. M. P. Terpugova, I. L. Kotlyarevskii, V. G. Mazur, and E. A. Martenko, Izv. Akad. Nauk SSSR, Ser. Khim., 602 (1973).
- 2. Yu. I. Amosov, I. L. Kotlyarevskii, and M. P. Terpugova, Inventor's Certificate No. 585161, 10.06 (1976); Byull. Izobr., No. 47 (1977).
- 3. A. A. Akhrem and Yu. A. Titov, Complete Synthesis of Steroids [in Russian], Nauka (1967), p. 77.
- 4. S. A. Ananchenko, A. V. Platonova, V. N. Leonov, and I. V. Torgov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1077 (1961).
- 5. F. Krollpfeiffer and W. Schäfer, Ber., 56, 620 (1923).

ANODE FLUOROALKYLATION OF FLUOROOLEFINS

V. A. Grinberg, V. R. Polishchuk,E. I. Mysov, L. S. German,L. S. Kanevskii, and Yu. B. Vasil'ev

UDC 541.13:542.944:66.095.253:547.413

Ethylene (1) and vinylidene fluoride (II) add $\dot{C}F_3$ radicals, generated during anodic oxidation of trifluoroacetate ion in aqueous MeCN, and form fluorine-containing hexanes as the principal products. In the case of (II), two molecules of olefin combine "head to head" to the extent of 95% [1].

> $CF_{3}COO^{-} - \bar{e} \rightarrow CF_{3}COO^{-} \rightarrow CF_{3} + CO_{2}$ $2\dot{C}F_{3} + 2CH_{2} = CX_{2} \rightarrow CF_{3}CH_{2}CX_{2} - CX_{2}CH_{2}CF_{3}$ X = H (I), F (II)

In the present work analogous reactions of 3,3,3-trifluoropropene (III), trifluoroethylene (IV), tetrafluoroethylene (V), and hexafluoropropene (VI) are studied.

A mixture of fluorooctanes $CF_3CH_2CH_-CHCH_3CF_3$ (95%, two diastereoisomers, separated by preparative F_3C CF₃

GLC) and isomeric $CF_3CHCH_2-CHCH_2CF_3$ (3%, identified by ¹⁹F NMR spectra) is obtained by electrolysis of $\begin{matrix} I \\ CF_3 \end{matrix}$

a solution of $CF_3COOH - CF_3COONa$ and (III) in aqueous MeCN at a current density of 2-4 A/dm² and an increase of pressure with a yield of 42% based on current. Traces of $(CF_3)_2CHCH_2CF_3$ and four isomeric products of $CF_3(C_3H_3F_3)_3CF_3$ are identified in the mixture by a chromatographic mass-spectrometric method (CMS).

Under analogous conditions compound (IV) forms a mixture of three isomeric dihydroperfluorohexanes with a 30% yield based on current: $CF_3CHFCF_2CF_2CHFCF_3$ (45% in mixture, preparative GLC), and also $CF_3CHFCF_2CHFCF_2CF_3$ and $CF_3CF_2CHFCHFCF_2CF_3$, which could not be separated; according to ¹⁹F NMR data, the content of the two latter substances in the mixture of isomers is 50% and 5%, respectively. In addition, a significant amount (6.3%) of $CF_3CHFCF_2CF_3$ and isomeric forms of $CF_3(C_2F_3H)_3CF_3$ are formed.

Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow. Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1056-1060, May, 1979. Original article submitted January 6, 1978. In the presence of (V) the electrolysis is complicated by polymerization. According to patent data [2], upon electrolysis of a mixture of CF_3COOH and (V) at a current density of $0.1-0.25 \text{ A/dm}^2$ polytetrafluoroethylene is obtained. A change to a higher current density (2-6 A/dm²) permits the 10% yield based on current of a mixture of $n-C_4F_{10}$ and C_6F_{14} in a ratio of 37:63 (NMR); however, under these conditions the primary products are C_2F_6 and a polymer, which forms a film on the surface of the anode. The formation of a film is also observed upon bubbling (V) through the electrolyte at atmospheric pressure.

Olefin (VI) is poorly active in the reaction under study. Even with a large excess of VI only traces of perfluoro-2-methylbutane form, which is the product of the addition of two CF_3 radicals to one molecule of ole-fin (NMR).

Electrolysis under the same conditions of MeCOOH-MeCOONa in the presence of (IV) or (VI) and also $MeOCO(CH_2)_4COOH-MeOCO(CH_2)_4COONa$ in the presence of (III) does not lead to the formation of addition products.

The formation of the products which are obtained can be described by the following general scheme:

$$2CF_3 \rightarrow CF_3CF_3 \tag{1}$$

$$CF_3 + C = C \longleftrightarrow CF_3 - C - C$$
(2)

$$CF_3 \rightarrow C - C + CF_3 \rightarrow CF_3 \rightarrow C - C - CF_3$$
(3)

$$2CF_{3} - C - C \rightarrow CF_{3} - (C - C)_{2} - CF_{3}$$

$$(4)$$

$$CF_{s}C-C + C=C \longleftrightarrow CF_{s}-C-C-C-C$$
 (5)

$$CF_3 - C - C - C + CF_3 - C - C - C - C - CF_3 - CF_3$$
(7)

$$CF_{3}-C-C-C + C = C + CF_{3}-(C-C)_{2}-C-C$$
(8)

$$CF_{3}-(C-C)_{2}-C-C+CF_{3}-CF_{3}-(C-C)_{3}-CF_{3}$$
(9)

The key stage is reaction (2), the initial attack of the olefin molecule by the CF_3 radical, which competes with the recombination of these radicals (in the gaseous phase at $25^{\circ}C$, $K_1 = 3 \cdot 10^9 \text{ dm}^3/\text{mole} \cdot \text{sec [3]}$). A sufficiently high yield of addition products indicates that in the reaction zone, i.e., on the anode surface or in immediate proximity to it, there is a high concentration of olefin. In favor of this conclusion is the fact that CF_3 radicals are almost completely spent in reactions (1) and (2) so that the product of reaction (3), the addition to one molecule of olefin, is not primary. It is significant that the rate of such products grows in proportion to the decrease of the activity of the olefin in reaction (2). If in the case of ethylene such a product does not appear even mass-spectrometrically, then (IV) already forms it with a noticeable yield, and in the case of (VI) it appears as the only product.

It is evident that other recombination processes of intermediately forming radicals with CF_3 , i.e., reactions (6) and (9), must not play an essential role during a deficiency of CF_3 radicals for a noticeable formation of products of reaction (3). Consequently, the growth of chains, with the exception of olefin (V), also proceeds only minimally, i.e., only reaction (5), but not (8), occurs, and basically, the recombination of initially forming radicals CF_3-C-C , i.e., reaction (4), is responsible for the formation of reaction products with the participation of the molecules of olefin.

This conclusion is also confirmed by the structure of the compounds produced. It is known that polar effects play the most important role in radical reactions of fluoroolefins, so that the electrophilic $\dot{C}F_3$ radical attacks (II) at 21°C to the extent of 96.5% [4], and (III) at 63°C, 99% [5] on the more hydrogenated C atom.

In accordance with this, the products of recombination of the initially forming radicals which we obtained consist of 95% (CF₃CH₂CF₂-)₂ in the case of (II) and (CF₃CH₂CH-)₂ in the case of (III). The by-product in both $\[black]_{CF_3}$

cases is an unsymmetrical radical, formed as the result of the recombination of a "normal" radical with an "abnormal" one, i.e., $CF_3CH_2CF_2CH_2CF_2CF_3$ (5%) and $CF_3CH_2CH-CH_2CHCF_3$ (3%). Consequently, 2.5% of the c_{F_4}

abnormal radical from (II) is formed and 1.5% from (III). These values are very close to those which are observed upon photochemical gas phase [3, 5] or liquid-phase thermal addition of $\dot{C}F_3$ to the indicated olefin (see [4]).

In the case of (IV) we obtained all three possible isomers of dihydroperfluorohexane: $CF_3CHFCF_2CF_2$ -CHFCF₃ (45%), $CF_3CHFCF_2CHFCF_2CF_3$ (50%), and $CF_3CF_2CHFCHFCF_2CF_3$ (5%). Proceeding from these relative amounts in the mixture and considering that in the given case the basic path of their formation is reaction (4), one can estimate that the mixture of initial fluoropropyl radicals consists of 70% CF_3CHFCF_2 and 30% CF_3CF_2CHF . According to data [5], upon gas-phase photoaddition of CF_3I to (IV) at 31°C the attack of CF_3 occurs on the CHF group to the degree of 73%.

The sharp decrease in the yield of addition products in the case of (VI) matches its comparatively low activity with respect to the CF_3 radical, consisting of only 1-3% in comparison with (I) [3]. Absence of a reaction of (IV) and (VI) with CH_3 can be connected with the large rate of recombination of these radicals in comparison with CF_3 (for $CH_3 k_1 = 10^{10} \text{ dm}^3/\text{mole} \cdot \text{sec}$ [6]).

Therefore, the behavior of fluoroolefins in reactions with $\dot{C}F_3$ radicals does not display any significant dependence on the manner of generation of the radicals, and under conditions of anodic oxidation of trifluoroacetate ions processes occur which are analogous to those observed during gas-phase and homogeneous liquidphase reactions. The latter evidently indicates the absence of strong adsorption of $\dot{C}F_3$ radicals on the surface of the Pt anode. This also indicates the fact which was established earlier by us, namely, the exchange of an atom of H on $\dot{C}F_3$ in derivatives of benzene under conditions where adsorption of the latter are not observed [7]. An analogous conclusion regarding cycloalkyl radicals was made during the study of the stereochemistry of the Kolbe electrosynthesis with participation of 4-tert-butylcyclohexanoic acid [8].

EXPERIMENTAL

The preparative electrolysis was conducted in a diaphragm-free high-pressure electrolyzer made of stainless steel with Pt electrodes. The anode surface is 16 cm². The electrolyte, consisting of 11.4 g CF₃-COOH, 40 ml MeCN, and 5 ml H₂O, was partially neutralized with 2.5 g Na₂CO₃ and sealed in a Teflon insert of 100 ml capacity, after which the electrolyzer was hermetically sealed, cooled with liquid N₂, evacuated, and a weighed content of olefin was condensed in it. After warming to ~20°C the electrolysis was conducted while the electrolyte was mixed with a magnetic stirrer.

After the electrolysis was complete, the gaseous products were collected in a cooled trap (-78° C), the electrolyzer was opened, the electrolyte was diluted with an aqueous solution of CaCl₂, the organic layer was separated, washed with H₂O, dried over MgSO₄, and distilled from concentrated H₂SO₄.

¹⁹F NMR spectra were taken on a Hitachi-Perkin-Elmer R-20 spectrometer, the chemical shifts were measured relative to external CF₃COOH, and the PMR spectra were taken on a Perkin-Elmer R-12 spectrometer. Mass spectra were obtained on a mass spectrometer with a Varian MAT CH-8 chromatograph (20% tricresyl phosphate on Shimalite). GLC analysis and preparative separation are performed on phase QF-1 (25% on Shimalite); the preparative chromatograph is a Carlo Erba model.

1. The electrolyzer is charged with 50 g of (III). The current density is 3 A/dm^2 , and the duration of electrolysis is 3.9 h. After conclusion of the experiment, 39 g of the original olefin is collected in the trap. From the electrolyte, 6.55 g (42%) of a liquid is obtained which contains (GLC, column temperature of 80°C) equal amounts of the two basic components (total 93%), traces of MeCN, and a series of impurities, of which the maximum is 5%.

According to chromatographic-mass-spectrographic data (original column temperature of 40°C; starting with the 5th minute, warming at the rate of 6 deg/min to 100°C), the mixture contains: original olefin, m/e 96 (M^+) ; $C_5H_3F_9$, m/e 215 (M - F), 195 $(M - HF_2)$, 175 $(M - H_2F_3)$, 145 $(M - CF_3)$; $C_8H_6F_{12}$ (one of the basic products), m/e 311 (M - F), 291 $(M - HF_2)$, 271 $(M - H_2F_3)$, 261 $(M - CF_4)$. Mass spectra of the second basic product and the majority of the impurities are analogous. MeCN, m/e 41 (M^+) ; four isomers of $C_{11}H_6F_{15}$, m/e 407 (M - F), 387 $(M - HF_2)$, 367 $(M - H_2F_3)$, 347 $(M - H_3F_4)$ also are characteristic products of further fragmentation.

Two basic components of the mixture are isolated at 70°C by preparative GLC. The first product has a mp 121-122°C (capillary). Found: 29.1% C; 2.1% H; 69.3% F. $C_{3}H_{6}F_{12}$. Calculated: 28.9% C; 2.4% H; 68.6% F. The second product has a mp 123-124°C. Found: 29.0% C; 2.4% H; 69.3% F. NMR spectra of both products are completely similar. The ¹⁹F NMR spectrum for the first: δ -11.1 br. t (J_{F-H} = 9.9 Hz) and -9.1 unresolved m, ratio 1:1. PMR spectrum: δ 2.55, 3.08 unresolved m, ratio 2:1.

The ¹⁹F NMR spectrum for the second: δ -11.1 br t. t (J = 10, J' = 2.6 Hz), -9.7 unresolved m, ratio 1:1. PMR spectrum: δ 2.51 d. (doublet constant, J' = 6.6 Hz).

On the basis of this data the indicated compounds are identified at two diastereoisomers of $(CF_3CH_2CH-)_2$.

Besides signals of the indicated substances, also found in the ¹⁹F NMR spectrum are a doublet δ -10.45, J = 10.4 Hz and a triplet δ -12.6, J = 7.2 Hz, 2:1 ratio, corresponding to the isomer CF₃CH₂CH_{(CF₃)CH₂CH-(CF₃)₂ (basic impurity with a 5% content). We could not find the signal of the third CF₃ group, evidently be-cause of overlap of signals of the basic components.}

2. The electrolyzer is charged with 30 g of (IV). The current density is 1.8 A/dm², and the duration of the electrolysis is 10 h. After conclusion of the experiment, 16 g of the original olefin is collected in the trap (withdrawn at temperature -40 to -50°C). The volatile liquid, remaining in the trap (0.7 g, 6.3%), is CF_3^{1} - $CHFCF_2CF_3^{2}$. The ¹⁹F NMR spectrum: δCF_3^{1} -2 unresolved m, δCF_3^{2} 7.1 d ($J_{CF_3^{2}-CF}$ = 10.3 Hz), δCH_2 49.5 (center of system AB), δCF 136. PMR spectrum: δ 5.23 (J_{CHF} = 44, J_{CH-CF_2} = 5.4, $J_{CH-CF_3^{1}}$ = 10.6 Hz).

From the electrolyte, 5.1 g (30% based on current) of liquid is obtained. According to GLC data (column temperature of 55°C), two basic components are contained in it in a 55:45 ratio; traces of MeCN and a series of impurities are also present. The following compounds are observed by the chromatographic mass-spectrographic method (original column temperature of 29°C, from the 10th minute, warming at the rate of 6 deg/ min to 120°C); C_4HF_9 , m/e 201 (M - F), 151 (M - CF₃), 132 (M - CF₄), 131 ($C_3F_5^+$), 119 ($C_3F_5^+$), 113 ($C_3HF_4^+$); $C_6H_2F_{12}$ (three isomers, of which two are basic components of the mixture) m/e 283 (M - F), 263 (M - HF₂), 243 (M - H₂F₃), 233 (M - CF₄), 213 (M - HF - CF₄), and other typical fragments. $C_8H_3F_{15}$ (two isomers), m/e 345 (M - HF₂), 325 (M - H₂F₃), 295 (M - HF - CF₃). Besides this, a series of compounds is observed whose mass spectra probably are not complete because of low concentration in the mixture. Some of the spectra contain ion peaks m/e 295 and their fragments, and possible, also correspond to the isomer $C_8H_3F_{15}$.

Two of the basic components of the mixture are isolated at ~20°C by preparative GLC. One of these is an individual compound, mp 82°C (capillary). Found: 23.9% C; 0.9% H; 75.9% F. $C_{g}H_{2}F_{12}$. Calculated: 23.8% C; 0.7% H; 75.5% F. The ¹⁹F NMR spectrum consists of unresolved multiplets, evidently due to overlapping of the signals of two diastereoisomers, $\delta = 1.8$, 47.1 (center of system AB), and 136, ratio of 3:2:1. PMR spectrum: δ 4.7, $J_{CHF} = 44$ Hz [corresponds to ($CF_{3}CHFCF_{2} = 1_{2}$].

The other isolated liquid is a mixture of two isomers. In the ¹⁹F NMR spectrum the proportion of integral intensities of signals of CF₃ groups, adjacent to CHF (two equal signals with δ -1.48 and -2.02, in each JCF₃-CF₂=JCF₃-CF=11.6, JCF₃-CH=6.2 Hz, correspond to two diastereoisomers of CF₃CHFCF₂CHFCF₂-CF₃) and CF₃ groups, adjacent to CF₂ (overlapping of several signals, position of the center δ 7.8) is equal to 147: 176. From this it follows that on CF₃ groups, belonging to the isomer (CF₃CF₂CHF-)₂, (176 - 147 = 29) conventional units of intensity fits and the relative content of this substance in the mixture, assuming the presence of two CF₃ groups, comprises ≈1/12. Thus, from the total content of 55% of CF₃CHFCF₂CHFCF₂CHFCF₂CF₃ and (CF₃CF₂CHF-)₂ in the original mixture, ~ 50.5% is from the first compound and ~4.5% from the second.

3. The electrolyzer is charged with 10 g of (V). The current density is 3 A/dm^2 , and the duration of the electrolysis is 4.5 h. In the trap, 1 g (10%) of volatile products is collected, distilled in the interval of 0-50°C. ¹⁹F NMR spectrum: $\delta \text{ CF}_2$ 50.9 (corresponding to n-C₄F₁₀ [9]). All groups are unresolved multiplets, the ratio of the integral intensities of the signals, corresponding to CF₂ groups of C₆F₁₄ and C₄F₁₀ is 63:37.

The electrolyte contains 1.4 g of a polymer. Liquid products could not be isolated from it.

4. The electrolyzer is charged with 32 g (VI), 50 ml CF₃COOH, and 2.5 g Na₂CO₃. The current density is 4 A/dm^2 , and the duration of the electrolysis is 4.5 h. In the trap, 27 g (VI) (withdrawn at temperature of $-15 \text{ to} -20^{\circ}\text{C}$) and 0.4 g (3.8%) of volatile liquid are collected. ¹⁹F NMR spectrum: $\delta -3.58$, t. (J_k = 11.4, J_t = 5.7 Hz), δ 4.66 d. (J_d = 12.9 Hz), δ 42.7 d.(J_d = 3.5 Hz), δ 128.2 unresolved m. The ratio of the integral intensities of signals is 6:3:2:1. The spectrum corresponds to perfluoro-2-methylbutane [10].

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 CF_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 CF_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, <u>71</u>, 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., <u>82</u>, 5831 (1960).

1,4 ADDITION TO A PERFLUORINATED

CROSS-CONJUGATED TRIENE

E. G. Ter-Gabriélyan, N. P. Gambaryan,

UDC 542.955:547.316.6'161

É. P. Lur'e, and P. V. Petrovskii

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.