REACTION OF FLUOROKETONES WITH VINYL ETHERS

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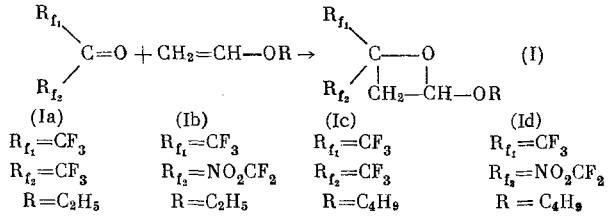
The well known ease of reaction of fluoroketones with olefins [1] permitted us to assume that the reaction with more nucleophilic vinyl ethers will proceed under rather mild conditions. However, according to the patent data [2], certain perfluoro- and chloroperfluoroketones, including hexafluoroacetone, react with vinyl ethers only when heated to 100°, forming a mixture of oxethane (I) and its linear isomer – the unsaturated carbinol (II).*

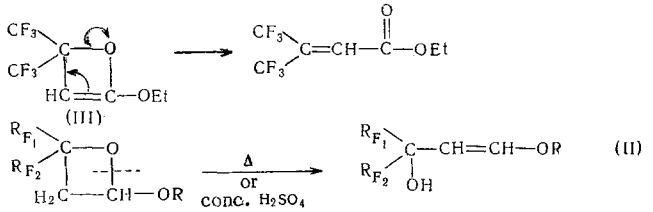
It was found that hexafluoroacetone reacts with vinyl ethers even at room temperature, forming only the primary reaction product – oxethane. Nitroperfluoroacetone, which is even more active, reacts at 0.5°.†



(Ia)	(Ib)	(Ic)	(Id)
$R_{f_1}=CF_3$	$R_{f_1}=CF_3$	$R_{f_1}=CF_3$	$R_{f_1}=CF_3$
$R_{f_2}=CF_3$	$R_{f_2}=NO_2CF_2$	$R_{f_2}=CF_3$	$R_{f_2}=NO_2CF_2$
$R=C_2H_5$	$R=C_2H_5$	$R=C_4H_9$	$R=C_4H_9$

The IR spectra of the oxethanes obtained do not contain absorption bands in the region of the C=C double bond and the OH of the hydroxyl group. The parameters of the PMR spectra of the oxethanes are presented in Table 1. We analyzed the three-spin system of the four-membered ring for a system of the type ABX. It is interesting to note the weakening of the electron density on the protons of the four-membered ring when one fluorine of the trifluoromethyl group is replaced by a nitro group.

The oxethanes (I) obtained, in contrast to the oxethanes (III), which isomerize even at room temperature, forming an α,β-unsaturated ester [6], isomerize only after prolonged heating to 100° or under the action of catalytic amounts of concentrated H_2SO_4, forming unsaturated carbinols (II).



(IIa)	(IIb)	(IIc)	(IId)
$R_{F_1}=CF_3$	$R_{F_1}=CF_3$	$R_{F_1}=CF_3$	$R_{F_1}=CF_3$
$R_{F_2}=CF_3$	$R_{F_2}=NO_2CF_2$	$R_{F_2}=CF_3$	$R_{F_2}=NO_2CF_2$
$R=C_2H_5$	$R=C_2H_5$	$R=C_4H_9$	$R=C_4H_9$

* We have found no examples of reactions of nonfluorinated ketones with vinyl ethers in the literature. Aldehydes, on the other hand, react with vinyl ethers when heated in the presence of acid catalysts (BF_3, BF_3 etherate, $ZnCl_2$, etc.), forming either 2,6-dialkyl-4-alkoxy-1,3-dioxanes [3] or β-alkoxyaldehydes and β-alkoxyketones [4], depending upon the nature of the aldehyde and catalysis.

† Perfluorocyclobutanone undergoes cyclodimerization at room temperature even with such a weak nucleophile as perfluoroalkylperfluorovinyl ether [5].

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 918-921, April, 1967. Original article submitted September 28, 1966.

TABLE 1

No.	R_{f_1}	R_{f_2}	R	Chemical shift of: δ(H¹)	δ(H²)	δ(H³)	δ (OCH₂)	δ (C—CH₂—C—)	δ (CH₃)	Spin-spin interaction constant, Hz: J (1,2)	J (1,3)	J (2,3)	J (CH₂—CH₂)	J (CH₂—CH₃)
Ia	CF_3	CF_3	C_2H_5	3.03	2.82	5.52	3.70	—	1.23	12.86	4.97	4.97	—	6.86
Ib	CF_3	CF_2NO_2	C_2H_5	3.21	2.99	5.54	3.68	—	1.24	15.42	5.14	5.14	—	6.86
Ic	CF_3	CF_3	C_4H_9	2.98	2.77	5.49	3.62	1.47	0.90	13.71	4.97	4.97	6.00	6.70
Id	CF_3	CF_2NO_2	C_4H_9	3.27	3.04	5.56	3.62	1.52	0.92	15.42	5.14	5.14	4.1	7.2

TABLE 2

No.	R_{f_1}	R_{f_2}	R	Chemical shift of: δ(H¹)	δ(H²)	δ (OH)	δ (OCH₂)	δ (—C—CH₂—C—)	δ (—CH₃)	Spin-spin interaction constant, Hz: J (1,2)	J (—CH₂—CH₂—)	J (—CH₂—CH₃)
IIa	CF_3	CF_3	C_2H_5	6.86	4.74	3.64	3.82	—	1.30	12.34	—	7.2
IIb	CF_3	NO_2CF_2	C_2H_5	6.83	4.71	3.65	3.81	—	1.29	12.84	—	6.7
IIc	CF_3	CF_3	C_4H_9	6.94	4.80	5.30	5.78	1.53	0.90	12.69	6.0	6.0
IId	CF_3	NO_2CF_2	C_4H_9	6.97	4.81	4.10	3.89	1.50	0.89	12.00	6.0	6.0

Distinct absorption bands in the region of the C=C double bond and the OH of the hydroxyl group appear in the IR spectra of the unsaturated carbinols (II). In the PMR spectra of the unsaturated carbinols (II) in weak magnetic fields, two doublets are observed, characteristic of a system of the type AB. The chemical shifts and spin-spin interaction constants of the unsaturated carbinols are cited in Table 2.

We had earlier utilized the catalytic decomposition of carbinols containing the nitrodifluoromethyl group at the α-carbon atom to synthesize trifluoromethyl ketones [1, 7]. The carbinol (IIb) undergoes an analogous decomposition.

$$NO_2CF_2-C(CF_3)(OH)-CH=CH-OC_2H_5 \xrightarrow[\Delta]{K_2CO_3} NO_2CF_2H + CF_3-C(=O)-CH=CH-OC_2H_5$$

(IIb) (IV)

The yield of the β-ethoxyvinyltrifluoromethyl ketone (IV) thereby formed is close to quantitative, and this reaction can be used as a convenient preparative method for synthesizing trifluoroalkyl-β-alkoxyvinyl ketones.

EXPERIMENTAL

The IR spectra were taken on the UR-10 instrument. The PMR spectra were taken on the "Hitachi H-60" instrument in a solution of CCl_4, using tetramethylsilane as the internal standard. The chemical shifts, cited in Tables 1 and 2, were measured in the δ-scale.

2-(Ethoxy-4,4,-bis(trifluoromethyl)oxethane (Ia). A mixture of 11.5 g hexafluoroacetone and 5 g ethylvinyl ether was sealed into a glass ampule. After half an hour, the reaction product was distilled off. Yield 14.9 g (90% of the theoretical) (Ia) with b.p. 57° (60 mm); n_D^{21} 1.3330. Found %: C 35.27; H 3.41; F 47.95. $C_7H_8F_6O_2$. Calculated %: C 35.29; H 3.36; F 47.90.

2-Ethoxy-4-trifluoromethyl-4-nitrodifluoromethyloxethane (Ib). To 28.9 g nitroperfluoroacetone, chilled to 0-5°, 10.8 g of ethylvinyl ether was added dropwise. Redistillation under vacuum yielded 27.8 g (70%) (Ib) with b.p. 54-56° (5 mm); n_D^{21} 1.3715. Found %: C 31.64; H 3.00; F 36.79. $C_7H_8F_5NO_3$. Calculated %: C 31.69; H 3.01; F 35.85.

2-Butoxy-4,4-bis(trifluoromethyl)oxethane (Ic). Into 5.8 g butylvinyl ether, placed in a flask equipped with a dry ice cooler, we passed 9.65 g of hexafluoroacetone. Redistillation under vacuum yielded 11.2 g (72.5%) (Ic) with b.p. 50-51 (10 mm); n_D^{22} 1.3525. Found %: C 40.59; H 4.53. $C_9H_{12}F_6O_2$. Calculated %: C 40.60; H 4.51.

2-Butoxy-4-trifluoromethyl-4-nitrodifluoromethyloxethane (Id). From 15 g nitroperfluoroacetone and 7.7 g butylvinyl ether, analogously to the product (Ib), we obtained 14.8 g (65%) of a liquid with b.p. 50-51° (2 mm); n_D^{18} 1.3835. Found %: C 36.25; H 4.19; F 32.17. $C_9H_{12}F_5N_1O_4$. Calculated %: C 36.86; H 4.096; F 32.08.

β-Ethoxyvinyl-bis(trifluoromethyl)carbinol (IIa). A 7-g portion of (Ia) was heated at 100° for 5 h. Redistillation under vacuum yielded 5 g (71.5%) (IIa) with b.p. 73° (30 mm); n_D^{20} 1.3550. Found %: C 35.26; H 3.52; F 48.00. $C_7H_8F_6O_2$. Calculated %: C 35.29; H 3.36; F 47.90. IR spectrum: 1675 (C=C), 3460 cm^{-1} (OH).

β-Ethoxyvinyltrifluoromethylnitrodifluoromethylcarbinol (IIb). A 2.3-g portion of (Ib) was heated in a sealed ampule at 100° for 3 h. Yield 1.8 g (78.2%) (IIb) with m.p. 50-51° (heptane). Found %: F 35.83; N 5.48. $C_7H_8F_5NO_4$. Calculated %: F 35.85; N 5.28. IR spectrum 1670 (C=C); 3360 (OH); 1360 and 1600 cm^{-1} (NO_2).

β-Butoxyvinyl-bis(trifluoromethyl)carbinol (IIc). To 4.5 g (Ic) we added two drops of concentrated H_2SO_4. After the exothermic reaction had ended, redistillation under vacuum yielded 3.6 g (80%) (IIc) with b.p. 42-44° (3 mm); $n_D^{19.5}$ 1.3720. Found %: C 40.26; H 4.49; F 42.89. $C_9H_{12}F_6O_2$. Calculated %: C 40.60; H 4.51; F 42.89. IR spectrum: 1680 (C=C); 3430-3500 cm^{-1} (OH).

β-Butoxyvinyltrifluoromethylnitrodifluoromethylcarbinol (IId). From 3.2 g (Id), analogously to product (IIc), we obtained 2.05 g (64%) (Id) with b.p. 74-75° (3 mm); n_D^{22} 1.4010. Found %: C 37.52; H 4.36; F 32.07. $C_9H_{12}F_5NO_4$. Calculated %: C 36.86; H 4.096; F 32.08. IR spectrum: 1665 (C=C): 3400-3550 (OH); 1360 and 1610 cm^{-1} (NO_2).

Trifluoromethyl-β-ethoxyvinyl ketone (IV). A 2.8-g portion of (IIb) was heated with a catalytic amount of potash at a temperature of 100-110°. Difluoronitromethane, identified by gas–liquid chromatography, was distilled off. Redistillation under vacuum yielded 1.7 g (96%) (IV) with b.p. 60° (23 mm); n_D^{25} 1.404. Found %: C 42.93; H 4.37; F 34.56. $C_6H_7F_3O_2$. Calculated %: C 42.85; H 4.16; F 33.92. IR spectrum: 1720 (C=O); 1600 cm^{-1} (C=C).

CONCLUSIONS

The reaction of perfluoroketones with alkylvinyl ethers leads to 2-alkoxy-4,4-bis(perfluoroalkyl) oxethanes, subsequent isomerization of which yielded β-alkoxyvinyl-bis(perfluoroalkyl)carbinols.

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