ON THE INTERACTION OF FLUORINATED KETONES WITH OLEFINS

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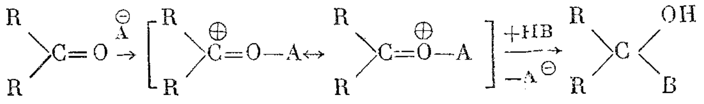
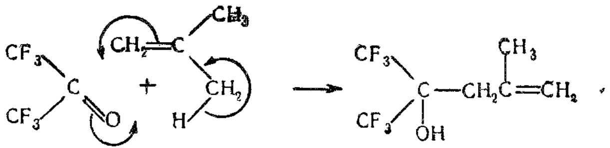
Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8,
pp. 1466-1469, August, 1965
Original article submitted November 20, 1964

Reactions in which a nucleophilic character of the carbonyl oxygen atom is manifested are rather typical of nonfluorinated ketones. The most widespread type of such reactions is the interactions of carbonyl compounds with weakly nucleophilic agents in the presence of acids (protonic or aprotonic). The first step in the reaction is activation of the carbonyl compound through its conversion to the "carboxonium" cation, the electrophilic properties of which are sufficient for interaction with weakly nucleophilic reagents:



As for fluorinated ketones, their electrophilic character is so great that they are capable of interacting with weak nucleophilic compounds under mild conditions without preliminary activation of the carbonyl group by acid catalysts. A well-known example of such interaction is the reaction of perfluorocyclobutanone with propylene, methylacetylene, and allene at room temperature, with the formation of unsaturated carbinols [1]. The less active perfluoroacetone reacts with olefins of the type of ethylene, propylene, and cyclohexene without heating only in the presence of aluminum chloride [2]. However, nitrous acid [3] and ketene [4] are added by hexafluoroacetone under mild conditions without preliminary activation of the ketone.

As was found, reactions of hexafluoroacetone with a number of olefins also do not require acid catalysis. Thus, hexafluoroacetone reacts exothermically with isobutylene at room temperature*



(I)

The reaction of hexafluoroacetone with methyl allyl ether proceeds under more rigorous conditions—with prolonged heating to 100°, while that with propylene proceeds with heating to 150°. Nitroperfluoroacetone, just as we should have expected, reacts even more actively with isobutylene, methyl allyl ether, and propylene. Thus, both the literature data and the results of our investigations show that in reactions of fluorinated ketones with weakly nucleophilic compounds, in a number of cases there is a characteristic "inversion" of the reaction mechanism: electrophilic addition (for nonfluorinated ketones) is converted to nucleophilic addition (for fluorinated ketones).

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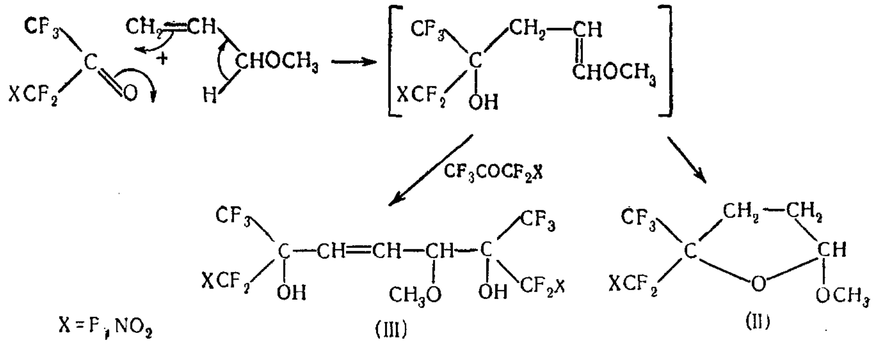
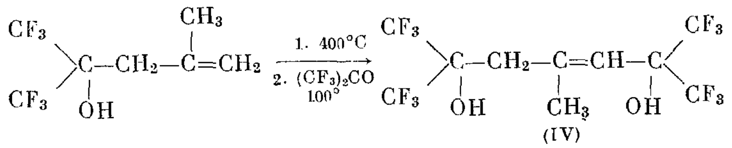
* The interaction of hexafluoroacetone with isobutylene was conducted earlier at 200°.



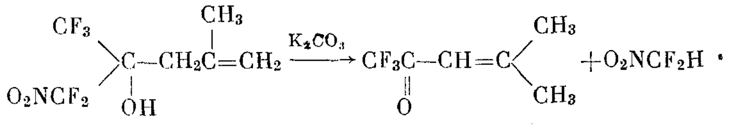
(III) (II)

The further transformations of the carbinols formed from the fluorinated ketones and olefins depend on the nature of the olefin and the fluorinated radical. The addition product of methyl allyl ether to perfluoroacetone and nitroperfluoroacetone, formed according to a scheme of six-membered cyclic transfer, i. e., with an allyl rearrangement [1, 5], could not be isolated, since as they are formed they are cyclized to tetrahydrofuran derivatives (II) or react with the following molecule of the carbonyl compound, being converted to unsaturated diols (III). Bis-(trifluoromethyl)isobutenylcarbinol (I) is also converted to an unsaturated diol when heated to 400°—1,3-bis-(2-hydroxyhexafluoroisopropyl)-2-methylpropene (IV). In the presence of catalytic amounts of potash, the diol (IV) is already formed at 200°. Obviously the carbinol (I) breaks down into the initial components under these conditions, while the hexafluoroacetone formed condenses with (I), which leads to the diol (IV). Actually, when hexafluoroacetone is heated with the carbinol (I) at 100°, the diol (IV) is formed in almost quantitative yield.



(IV)

Nitropentafluorodimethylisobutenylcarbinol, in contrast to (I), is converted to difluoronitromethane and trifluoromethyl-β,β-dimethylvinyl ketone (V), the structure of which was demonstrated by the proton NMR spectrum, when heated with catalytic amounts of potash even on a water bath. Thus, the "haloform" decomposition of this carbinol is accompanied by a prototropic allyl rearrangement:



(V)

EXPERIMENTAL SECTION

Interaction of Fluorinated Ketones with Olefins. Isobutylene. A mixture of 4.15 g of hexafluoroacetone and 4 ml isobutylene was left overnight in a sealed ampoule. Distillation produced 5.4 g (97% of the theoretical) of (I); b. p. 113-115°; n_D^{20} 1.3485. Literature data [2]; b. p. 113°, n_D^{20} 1.3470. IR spectrum: 1655 cm^{-1} (C = C), 3088 cm^{-1} (= CH_2). Dibromide of the carbinol (76%), b. p. 69-70° (6 mm); n_D^{19} 1.4349; d_4^{19} 1.918. Found: C 21.43; H 2.16; F 29.68%; MR 51.93. $C_7H_8F_6Br_2O$. Calculated: C 21.99; H 2.09; F 29.82%; MR 52.42. Tribromide—m.p. 50-51° (from hexane). Found: C 18.03; H 1.49; F 24.98; Br 52.75%. $C_7H_7F_6Br_3O$. Calculated: C 18.22; H 1.52; F 24.73; Br 52.06%.

Analogously, nitropentafluorodimethylisobutenylcarbinol was produced from nitroperfluoroacetone and isobutylene in 96% yield; b. p. 53-54° (14 mm); n_D^{20} 1.3847; d_4^{20} 1.404. Found: C 33.52; H 3.06; F 37.65; N 5.7% MR 41.9. $C_7H_8F_5NO_3$. Calculated: C 33.74; H 3.21; F 38.55; N 5.62%; MR 41.55. IR spectrum: 1650, 3085 cm^{-1}. In the proton NMR spectrum, the carbinol gives four signals with area ratio 2:1:2:3. Values of the chemical shifts (from benzene): $23.5 \cdot 10^{-7}$ (doublet = CH_2), $36 \cdot 10^{-7}$ (OH), $46.2 \cdot 10^{-7}$ (CH_2), $55 \cdot 10^{-7}$ (CH_3).

Propylene. A mixture of 6 g of hexafluoroacetone and 3.6 ml of propylene was heated in a sealed ampoule for nine hours at 150°. Distillation produced 5 g (67% of the theoretical) of bis(trifluoromethyl)allylcarbinol; b. p. 95-98°; n_D^{20} 1.3345. Literature data [2]: b. p. 40° (100 mm); n_D^{20} 1.3400. The reaction does not proceed at 100°.

When nitroperfluoroacetone was heated with propylene to 100° for six hours, nitropentafluorodimethylallylcarbinol was obtained in 66% yield: b. p. 54-55° (20 mm); n_D^{20} 1.3780; d_4^{20} 1.3212. Found: F 41.26; N 6.34%; MR 37.29. $C_6H_6F_5NO_3$. Calculated: F 40.17; N 5.98; MR 37.28.

Methyl allyl ether. A mixture of 10.2 g of hexafluoroacetone and 8 g of methyl allyl ether was heated in a sealed ampoule for 20 h at 100°. Distillation isolated 2.8 g (18% of the theoretical) of 1,1-bis(trifluoromethyl)-4-methoxytetrahydrofuran; b. p. 52° (95 mm); n_D^{20} 1.342. Found: C 34.41; H 3.30; F 47.09%. $C_7H_8F_6O_2$. Calculated: C 35.3; H 3.32; F 47.9% and 8.2 g (60% of the theoretical) methyl-1, 3-bis(2-hydroxyhexafluoroisopropyl)-allylether; b. p. 57-58° (7 mm); m.p. 86-87° (from heptane). Found: C 30.15; H 1.98; F 55.34%. $C_{10}H_8F_{12}O_3$. Calculated: C 29.89; H 1.98; F 56.4%.

Analogously, after heating for 10 h at 100°, the following were produced from nitroperfluoroacetone: 1,1-nitropentafluorodimethyl-4-methoxytetrahydrofuran (30% yield); b. p. 50° (6 mm); n_D^{20} 1.3811. Found: C 31.63; H 2.99; N 5.16%. $C_7H_8F_5NO_4$. Calculated: C 31.7; H 3.05; N 5.28%; methyl-1,3-bis(2-hydroxynitroperfluoroisopropyl)allyl ether (42% yield); m. p. 89-90° (from heptane). Found: C 25.97; H 1.79; F 41.34% . $C_{10}H_8F_{10}N_2O_7$. Calculated: C 26.2; H 1.75; F 41.42%.

1,3-Bis-(2-hydroxyhexafluoroisopropyl)-2-methylpropane (IV). A mixture of 5 g (I) and 3.7 g hexafluoroacetone was heated in a sealed ampoule for 24 h at 100°. Yield 8.1 g (93% of the theoretical) (IV); m.p. 144° (from benzene). Found: C 31.24; H 2.19; F 58.55%. $C_{10}H_8F_{12}O_2$. Calculated: C 30.92; H 2.06; F 58.76%. (IV) was also produced by heating the carbinol (I) at 400° or by heating to 200° in the presence of catalytic amounts of potash.

Trifluoromethyl-β, β-dimethylvinyl ketone (V). 23.2 g of nitropentafluorodimethylisobutenylcarbinol was heated at 100° in the presence of catalytic amounts of potash. In this case, 7.4 g (82% of the theoretical) of nitrodifluoromethane, b. p. 44-45°, was distilled off; the product was identified by gas-liquid chromatography. Distillation of the residue isolated 6.8 g (48% of the theoretical) (V); b. p. 110-111°; n_D^{20} 1.3836; d_4^{20} 1.272. Found: C 46.93; H 4.48; F 36.93%. $C_8H_7F_3O$. Calculated: C 47.3; H 4.6; F 37.5%. In the proton NMR spectrum, (V) gives two signals with an intensity ratio of 6:1.

CONCLUSIONS

The reaction of fluorinated ketones with a number of olefins was studied.

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