# REACTION OF HEXAFLUOROACETONE WITH ACETIC ANHYDRIDE

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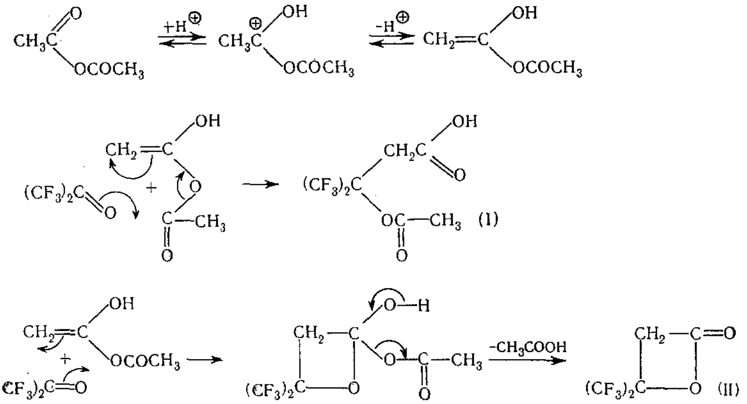
It is known that perfluoro aldehydes [1], and also chloral [2], form alkylidene diacetates when reacted with acetic anhydride in the presence of sulfuric acid, in this respect not differing from ordinary carbonyl compounds [3, 4].

It proved that hexafluoroacetone reacts in a completely different manner with acetic anhydride. β-Acetoxy-β,β-bis(trifluoromethyl)propionic acid (I) and β,β-bis(trifluoromethyl)-β-propiolactone* (II) are formed when the reactants are heated for a long time with catalytic amounts of sulfuric acid.

Such an unexpected reaction result can be explained by the lowered nucleophilicity of the oxygen in the C = O group of hexafluoroacetone [6], hindering its attack by the acetyl cation. Besides this, because of the exceedingly high electrophilicity of hexafluoroacetone, it becomes possible for it to react with acetic anhydride in the same manner as with a compound containing an active methylene group (see [7]). Starting with this, the formation of the reaction products can be depicted in the following manner.



By means of special experiments it was shown that under the reactions, at 100°, acetoxy acid (I) does not form lactone (II), although in the pyrolysis of (I), together with β,β-bis(trifluoromethyl)acrylic acid, a certain amount of lactone (II) is also formed, in which connection its yield increases if the pyrolysis is run in the presence of catalytic amounts of sulfuric acid. Besides this, it was established that lactone (II) reacts with acetic acid to give acetoxy acid (I). These data indicate that in the reaction either lactone (II) is formed first, undergoing partial transformation to acid (I), or else the formation of acid (I) and lactone (II) goes independently.

As a result, when acetic anhydride is reacted with hexafluoroacetone in the presence of sulfuric acid it acts, not as an acetylating agent, but as a compound with an active methylene group. This sharply differentiates hexafluoroacetone from other carbonyl compounds†.

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*Lactone (II) was obtained previously [5] by the reaction of hexafluoroacetone with ketene and dehydration of the β-hydroxy-β,β-bis(trifluoromethyl)propionic acid.

†It is possible that carbonyl cyanide [8] reacts with acetic anhydride in the same manner as does hexaflufluoroacetone. In this case a compound of composition $C_5H_2O_2N_2$ was obtained, which corresponds either to β,β-dicyano-β-propiolactone or to β,β-dicyanoacrylic acid. However, the structure of this compound was not established.

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## EXPERIMENTAL

β-Acetoxy-β,β-bis(trifluoromethyl)propionic Acid (I) and β,β-bis(trifluoromethyl)-β-propiolactone (II). A mixture of 24 g of hexafluoroacetone, 16.3 g of acetic anhydride and several drops of $H_2SO_4$ was heated in a steel ampule for 33 h at 100°. Fractional distillation of the reaction mass gave 7.7 g (25.6% of theory) of β-lactone (II), b.p. 95-98%; $n_D^{20}$ 1.3240.* Based on the data given in [5]: b.p. 94-95°, $n_D^{20}$ 1.3240. From the residue, after recrystallization from benzene, we obtained 16.6 g (43% of theory) of the β-acetoxy acid (I), m.p. 97-98°. Found: C 31.5; H 2.3; F 42.4%. $C_7H_6F_6H_4$. Calculated: C 31.3; H 2.25; F 42.5%.

A mixture of 3.55 g of β-lactone (II), 2 ml of glacial acetic acid and a drop of $H_2SO_4$ was heated for 37 h at 100°. The unreacted lactone (0.43 g) was distilled off. From the residue, after recrystallization from benzene, we obtained 2.2 g (55% of theory) of acid (I), m.p. 94-96° (the mixed melting point with the authentic material is not depressed).

A mixture of 5.6 g of β-hydroxy-β,β-bis(trifluoromethyl)propionic acid and 6 g of acetic anhydride was heated for 27 h at 100°, after which the mass was poured into water, and the precipitate was filtered and dried. We obtained 5.17 g (78% of theory) of (I), m.p. 95-98° (from benzene).

A solution of 0.44 g of (I) in 10% NaOH solution was allowed to stand for 4 days, after which it was acidified and extracted with ether to give 0.2 g (54% of theory) of β-hydroxy-β,β-bis(trifluoromethyl)propionic acid, m.p. 86-88° (from $CCl_4$) (the mixed melting point with the authentic material is not depressed) [5].

Decomposition of β-Acetoxy-β,β-bis(trifluoromethyl)propionic Acid (I). A mixture of 7.7 g of β-acetoxy acid (I) and 2 drops of $H_2SO_4$ was heated at 180-200° in a flask fitted with a descending condenser. The distillate with b.p. 105-165° was collected, which after fractional distillation gave 3.5 g of a fraction with b.p. 94-120°, containing 2.9 g (47% of theory) of lactone (II), and 1.7 g of the β,β-bis(trifluoromethyl)acrylic acid fraction with b.p. 150-165°, from which after esterification we isolated the ethyl ether of this acid, identified with the authentic material [9] by gas — liquid chromatography. The pyrolysis of acid (I) in the absence of $H_2SO_4$ gave the lactone in 23% yield.

A mixture of 9.9 g of acetoxy acid (I), 3 ml of acetic anhydride and 2 drops of $H_2SO_4$ was heated for 37 h at 100°. β-Lactone (II) was not found in the reaction mass. 7.8 g (79% of theory) of the starting acid was recovered.

## CONCLUSIONS

When acetic anhydride reacts with hexafluoroacetone it acts not as an acetylating agent, but as a compound containing an active methylene group.

## LITERATURE CITED

1. D. R. Husted and A. H. Ahlbrecht, J. Amer. Chem. Soc., 74, 5422 (1952).
2. E. H. Huntress, Organic Chlorine Compounds, New York (1948), p. 637.
3. E. H. Man, J. J. Sanderson, and C. R. Hauser, J. Amer. Chem. Soc., 72, 847 (1950).
4. I. V. Machinskaya, V. A. Barkhash, and V. I. Molchanov, Zh. obshch. khimii, 23, 756 (1953).
5. I. L. Knunyants and Yu. A. Cheburkov, Izv. AN SSSR, Otd. khim. Nauk, 1960, 678.
6. I. L. Knunyants, Tsin-Yun Chen, N. P. Gambaryan, and E. M. Rokhlin, Zh. Vses. khim. Obshchestva im. Mendeleeva, 5, 114 (1960).
7. C. R. Hauser, F. W. Swamer, and J. T. Adams, Monograph "Organic Reactions" [Russian translation], 8, IL, Moscow (1956), p. 129.
8. R. Malachowski, Roczniki Chem., 24, 229 (1950).
9. I. L. Knunyants and Yu. A. Cheburkov, Izv. AN SSSR, Otd. khim. Nauk, 1960, 2162.

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*Here and below, lactone (II) was identified by conversion to the anilide of β-hydroxy-β,β-bis(trifluoromethyl)propionic acid [5].