DECAFLUOROHYDROBENZOIN

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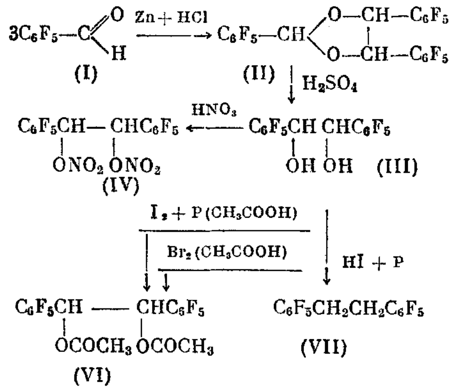
As is known, pentafluorobenzaldehyde (I) displays a number of anomalies in chemical behavior. Thus, under the conditions of the Cannizzaro reaction it undergoes cleavage with the formation of pentafluorobenzene and formic acid [1]; it was shown by us that (I) does not enter into the benzoin condensation under the influence of KCN in aqueous alcohol medium, etc.

In the present study we found that the reduction of (I) with zinc and hydrochloric acid smoothly yields the acetal (II) of pentafluorobenzaldehyde and decafluorohydrobenzoin (III); benzaldehyde under the same conditions gives hydrogenzoin in good yield [2]. We were unable to obtain (III) even when (I) was added slowly to a mixture of zinc and hydrochloric acid, i.e., under conditions where excess (I) was not present in the reaction medium. As a result, the rate of the acetalization of (I) is very high, and evidently it is much faster than the rate of its reduction. This tendency toward acetalization is explained by the high electrophilicity of the carbonyl group in (I). The previously unknown decafluorohydrobenzoin (III) was isolated by us when (II) was hydrolyzed with aqueous—alcoholic H_2SO_4 solution; the presence of (I) in the hydrolysis products was established by preparing its 2,4-dinitrophenylhydrazone, which was identical with the authentic sample. Glycol (III) displays a number of anomalies in chemical behavior when compared with hydrobenzoin. Thus, the hydroxyl groups in (III) are not replaced by halogen when (III) is reacted with PCl_3, PCl_5, or PBr_5; (III) is not dehydrated when heated with oxalic acid or with 20% H_2SO_4 solution (diphenylacetaldehyde is obtained in good yield from hydrobenzoin under these conditions [3, 4]), which testifies to the great stability of the C–O linkage and the difficulty of forming the transition state, possessing the character of the carbonium ion. (III) is quite resistant toward oxidation; thus, it is not oxidized by HNO_3 (d 1.4), either in the cold, or on long refluxing; at the same time hydrobenzoin is oxidized by HNO_3 (d 1.36) to benzoin even in the cold [5]. The treatment of (III) with nitric acid (d 1.5), both in the cold and when heated, gave us an unusual product — the dinitrate of decafluorohydrobenzoin (IV) in up to 91.5% yield; the analogous ester of hydrobenzoin is not known.



It is interesting to mention that the ability to give nitrates when treated with NHO_3 (d 1.5) is, in general, apparently inherent to a secondary alcohol group found in series with a pentafluorophenyl moiety. Thus, the treatment of decafluorobenzhydrol with NHO_3 (d 1.5) in the cold also gave the nitrate in 75.8% yield.

When (III) was oxidized with bromine in glacial acetic acid (here hydrobenzoin is converted to benzil [6]) we isolated the glycol diacetate (VI); this same product was also obtained when (III) was reduced with iodine and phosphorus in glacial acetic acid (decafluorobenzhydrol gives decafluorodiphenylmethane in good yield under these conditions [7]). (VI) was also isolated by us in good yield by the direct reaction of (III) with glacial acetic acid. We were able to reduce (III) to the symmetrical decafluorodiphenylethane (VII) only by heating at 200°C with HI and phosphorus; (VII) proved to be identical with the authentic sample, obtained from pentafluorobenzyl chloride and magnesium.

EXPERIMENTAL[*]

Decafluorohydrobenzoin (III). Into a flask were charged a solution of 10 g of pentafluorobenzaldehyde (I) in 10 ml of ethyl alcohol and 3 g of activated zinc turnings. With vigorous stirring, in a N_2 stream, a solution of 9 g of concentrated HCl in 7 ml of alcohol was added slowly, and the mixture was refluxed for 2-3 h. Then the cooled mixture was poured into 60 ml of water, and the precipitate was filtered and washed with aqueous alcohol. We obtained 8 g (78%) of acetal (II); m.p. 144.5-146° (from alcohol). Found %: C 44.16; H 0.49; F 49.85. Mol. wt. 572. $C_{21}H_3O_2F_{15}$. Calculated %: C 44.0; H 0.52; F 49.98. Mol. wt. 572. Infrared spectrum (in CCl_4), cm^{-1}: 1530 s (fluorinated aromatic ring), 990 s (C–F). λ_{max} (in C_2H_5OH) 264 mμ (log ε 3.188).

To a solution of 1.7 g of acetal (II) in 28 ml of alcohol, obtained by heating, was added a mixture of 14 ml of concentrated H_2SO_4, 10 ml of alcohol,and 10 ml of water, and the mixture was refluxed for 2 h. After cooling, the solution was neutralized with solid sodium carbonate, diluted with water, filtered, and the precipitate was washed repeatedly with ether; the filtrate was evaporated, the residue was extracted with ether, and the ether layer was washed first with $Na_2S_2O_5$ solution and then with water. The precipitate obtained after distilling off the ether was washed with hot petroleum ether. We obtained 0.96 g (82%) of (III), m.p. 184-185° (from benzene). Found %: C 42.55; H 1.02; F 48.32. Mol. wt. 401. $C_{14}H_4O_2F_{10}$. Calculated %: C 42.60; H 1.02; F 48.15. Mol. wt. 394. Infrared spectrum (in KBr – 400-1800 cm^{-1}, in a mixture of perfluoroalkanes – 2500-3800 cm^{-1}): 992 s (C–F), 1510 s and 1530 s (fluorinated aromatic ring), 3470 broad (OH). λ_{max} (in C_2H_5OH) 262 mμ (log ε 3.114).

Dinitrate of Decafluorohydrobenzoin (IV). 1 g of decafluorohydrobenzoin was mixed with 8 ml of concentrated HNO_3 (d 1.5) at –5 to –10° and kept at this temperature for 1 h. Then it was poured into 50 ml of ice water, and the precipitate was filtered and washed with water until neutral. We obtained 1.12 g (91.5%) of (IV), m.p. 138-141° (from alcohol). Found %: C 34.86; H 0.86; F 39.45; N 5.74. $C_{14}H_2O_6F_{10}N_2$. Calculated %: C 34.81; H 0.42; F 39.40; N 5.79. Infrared spectrum (in KBr), cm^{-1}: 1000 s (C–F), 1290 s and 1660 s ($-O-NO_2$), 1525 s (fluorinated aromatic ring). λ_{max} (in $CHCl_3$) 266 mμ (log ε 3.27).

Nitrate of Decafluorobenzhydrol (V).[†] A mixture of 1 g of decafluorobenzhydrol and 4.4 ml of HNO_3 (d 1.5) was allowed to stand at room temperature for a day. Then it was poured into 40 ml of water, extracted with ether, and the ether layer was washed with sodium carbonate solution and then with water, and dried over $MgSO_4$. After distilling off the ether the residue was fractionally distilled in vacuo to give 0.88 g (78.5%) of (V), b.p. 124.7-124.8° (3.5 mm); $n_D^{22.5}$ 1.4702. Found %: C 37.97; H 0.48; F 46.59; N 3.54. $C_{13}HO_3F_{10}N$. Calculated %: C 38.14; H 0.24; F 46.45; N 3.42. Infrared spectrum (neat), cm^{-1}: 1010 s (C–F), 1290 and 1670 s ($-O-NO_2$), 1525 s (fluorinated aromatic ring). λ_{max} (in C_2H_5OH) 264 mμ (log ε 3.246).

Diacetate of Decafluorohydrobenzoin (VI). A mixture of 0.43 g of decafluorohydrobenzoin and 9 g of glacial acetic acid was refluxed for 35 h. The solution was poured into 10 ml of water. The obtained precipitate was filtered and washed with water until neutral. We obtained 0.42 g (80.7%) of (VI), m.p. 162-163° (from alcohol). Found %: C 45.38; H 1.49; F 39.14. $C_{18}H_8O_4F_{10}$. Calculated %: C 45.18; H 1.67; F 39.74. Infrared spectrum (in CCl_4), cm^{-1}: 1755 s (C=O in acetates), 1520 s (fluorinated aromatic ring), 1005 s (C–F). λ_{max} (in C_2H_5OH) 264 mμ (log ε 3.158).

1,2-Bis(pentafluorophenyl)ethane (VII). A mixture of 1.11 g of decafluorohydrobenzoin, 0.28 g of red phosphorus and 1.21 g of concentrated HI was heated in a sealed tube at 200-210° for 7 h. The

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[*] E. V. Lugovska assisted in the experimental portion of the work.

[†] It is interesting to mention that the benzhydrol nitrate obtained from diphenylbromomethane and silver nitrate is very unstable and decomposes at room temperature [8].

mixture was treated with water, extracted with ether, and the ether extracts were washed with $Na_2S_2O_5$ solution and then with water, and dried over $MgSO_4$. After distilling off the ether we obtained 0.8 g (78.8%) of (VII) with m.p. 102-104° (from alcohol). Literature data [9]: m.p. 104°. Found %: C 46.41; H 1.21; F 51.94. $C_{14}H_4F_{10}$. Calculated %: C 46.40; H 1.10; F 52.48. Infrared spectrum (in CCl_4), cm^{-1}: 1510 and 1520 s (fluorinated aromatic ring), 980 and 990 s (C–F). λ_{max} (in C_2H_5OH) 282 mμ (log ε 4.318).

CONCLUSIONS

Decafluorohydrobenzoin was synthesized and some of the anomalies in its chemical behavior were described.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.