REACTION OF PERFLUORODIBENZOYLMETHANE WITH HYDRAZINES

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Previously we had shown that polyfluoroaromatic β-diketones, which are capable of enolization, form stable isolatable salts when treated with free hydrazine bases. The character of the reaction of these β-diketones with hydrazine salts is quite dependent on the nature of the substituent in the methylene group of the β-diketone. In the present paper we studied the reaction of the first described member of the perfluorinated aliphatic–aromatic β-diketones, namely perfluorodibenzoylmethane (I) [1] with phenylhydrazine (II), hydrazine (III), and also their salts $NH_2NHR \cdot HA$ [R = Ph, A = OAc (IV); R = H, A = OAc (V)].

The reaction of equimolar amounts of ketone (I) and base (II) in CCl_4 medium, with cooling to 0°C, gave a product (VI) of composition $C_{21}H_{10}F_{12}N_2O_3$ in 74% yield, which product proved to be very unstable both in solutions and in the solid state. The IR spectra of compound (VI) as a KBr pellet, in CD_3OD, and as a mull in perfluorokerosine, resemble each other in the 1500-1800 cm^{-1} region, and do not contain the absorption bands of the carbonyl group. The IR spectrum of the mull of the sample in perfluorokerosine contains a narrow absorption band at 3557 cm^{-1} (OH) and a broad band at 3200 cm^{-1} (NH). The F^{19} NMR spectrum (tetrahydrofuran) contains the signals of two nonequivalent C_6F_5 groups and a CF_2 group (system AB). A mixture of the monophenylhydrazone of perfluorodibenzoylmethane (VII) and 1-phenyl-3,5-bis-pentafluorophenyl-4,4-difluoro-5-hydroxypyrazoline (VIII) (44 and 19%) is obtained when compound (VI) is refluxed in alcohol. A similar result is also obtained when a mixture of equimolar amounts of ketone (I) and base (II) is refluxed under the same conditions. The structure of compounds (VII) and (VIII) is confirmed by the spectra data. In the F^{19} NMR spectrum of hydrazone (VII) are present the signals of two nonequivalent C_6F_5 groups, while the signal of the CF_2 group represents a triplet of triplets (J 9.5 and 7 Hz). The structure of hydrazone (VII) is confirmed by the data of the IR spectrum (CCl_4): 1600 s (C=N), 1735 s (C=O), and 3335 w cm^{-1} (NH). In the IR spectrum of compound (VIII) is absent absorption that is characteristic for the C=O group, but absorption is present at 3590 cm^{-1} (OH). The F^{19} NMR spectrum (CCl_4) contains the signals of two nonequivalent C_6F_5 groups and of aliphatic fluorine nuclei (system AB). The NMR spectrum (CCl_4) exhibits a multiplet at −7.0 (Ph), and a broad signal at −3.75 ppm (OH); the latter disappears in the spectrum after shaking the solution with D_2O. When hydrazone (VII) and pyrazoline (VIII) are refluxed in alcohol, under the conditions used to obtain the mixture of these compounds from product (VI), their mutual interconversion is not observed. Cleavage of ionic fluorine occurs when base (II) is reacted with hydrazone (VII) and with pyrazoline (VIII) under the same conditions. The mutual interconversion of compounds (VII) and (VIII) was also not detected when each of these compounds was kept for 6 min (the time required to convert compound (VI) to a mixture of the indicated compounds when refluxed in alcohol) at 125°. As a result, both compounds (VII) and (VIII) are formed from compound (VI). On the basis of the data of the analyses, the spectra, and the described chemical transformations, we propose for compound (VI) the formula 1-phenyl-3,5-bis-pentafluorophenyl-3,5-dihydroxy-4,4-difluoropyrazolidine hydrate. In the mother liquor, after the removal of (VI), can be isolated a small amount of hydrazone (VII). At the same time, when a mixture of equimolar amounts of ketone (I) and base (II) was refluxed, or when compound (VI) was refluxed in CCl_4, followed by dissolving compound (VI) in acetic acid and subsequent dilution of the solution with water, and also when acetate (IV) was reacted with ketone (I), only hydrazone (VII) was obtained (94-97%).

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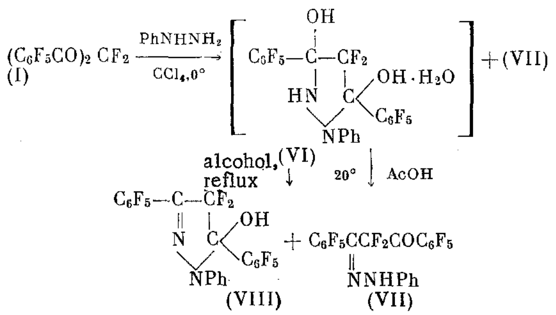
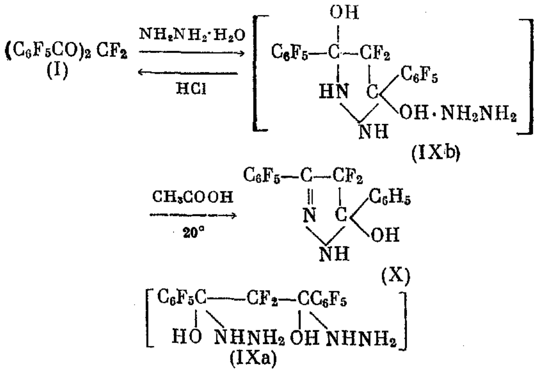


A practically equimolar mixture of the starting (I) and a product (IX) of composition $C_{15}H_8F_{12}N_4O_2$ is formed when equimolar amounts of ketone (I) and base (III) are reacted in alcohol. When the ratio of ketone to base is 1 : 2 the yield of product (IX) increases up to 96%. In the IR spectrum of the latter (perfluorokerosine) is absent the absorption band of the carbonyl group, but a broad absorption band is present at 2850-3370 cm^{-1}. Treatment of compound (IX) with conc. HCl gives the starting ketone (I) (99%), whereas dissolving compound (X) in acetic acid and subsequent dilution of the solution with water fail to give the starting ketone (I), and instead 3,5-bis-pentafluorophenyl-4,4-difluoro-5-hydroxypyrazoline (X) is formed (95%). The structure of the latter was confirmed by the spectral data: the IR spectrum (CCl_4) contains the absorption bands of the NH and OH groups (3420 and 3600 cm^{-1}), while the F^{19} NMR spectrum shows the resonance absorption of two nonequivalent C_6F_5 groups and the CF_2 group (system AB). Pyrazoline (X) is also formed when ketone (I) is reacted with acetate (V) at room temperature (90%), and also when a mixture of ketone (I) and base (III) is refluxed in alcohol (92%). Compound (IX), on the basis of the data of the analyses and the IR spectra, can have the structure of either the bis-geminal product (IXa) or of the hydrazinium salt of 3,5-bis-pentafluorophenyl-3,5-dihydroxy-4,4-difluoropyrazolidine (IXb) (cf. [2]). The fact that the treatment of this compound with acetic acid in the cold gives pyrazoline (X) makes the formula of pyrazolidine (IXb) to be preferred.

As a result, a high electrophilicity of both C = O groups is manifested in the reactions of compound (I) with bases (II) and (III), which leads to the formation of mainly the corresponding pyrazolines; at the same time, nucleophilic substitution of the fluorine in the ring fails to occur, which is the main process in the reactions of these bases with polyfluoroaromatic monocarbonyl compounds [3]



EXPERIMENTAL METHOD

The IR spectra were taken on a UR-20 instrument for 5% solutions, and also as KBr pellets. The UV spectra were taken on a Unicam SP-700c instrument, and the molecular concentration was 10^{-4}. The H^1 and F^{19} NMR spectra were taken on a Varian A-56/60-A instrument, the values of the chemical shifts are given on the δ scale, and the internal standards were respectively hexamethyldisiloxane and hexafluorobenzene.

Reaction of Ketone (I) with Phenylhydrazine (II). A solution of 0.11 g of base (II) in 1.6 ml of CCl_4, cooled to 0°C, was added in drops, with stirring and cooling in ice, to a solution of 0.44 g of ketone (I) in 1.6 ml of CCl_4. The precipitate was suction-filtered and washed with CCl_4. We obtained 0.42 g (74%) of compound (VI), mp 103-105° (decompn.). λ_{max} (alcohol) 244 and 348 nm (log ε 4.09 and 3.42). F^{19} NMR spectrum (tetrahydrofuran, 55%): −0.4 ($4F_m$), −9.0 (F_p), −10.0 (F_p), −25.2 ($2F_o$), −28.4 ($2F_o$), −41.7, and −50.0 ppm (CF_2, J_{FF} 225 Hz). Found: C 44.49, 44.62; H 1.58, 1.58; F 40.83, 41.03; N 4.45, 4.48%. $C_{21}H_{10}F_{12}N_2O_3$. Calculated: C 44.53; H 1.78; F 40.26; N 4.94%.

The solvent was removed from the mother liquor of product (VI). We obtained 0.11 g (21%) of hydrazone (VII), mp 119-120° (from petroleum ether). λ_{max} (heptane): 282 and 309 nm (log ε 4.04 and 4.10). NMR (CCl_4, 15%): multiplet at −7.00 (Ph) and a broad signal at −7.65 ppm (NH). F^{19} NMR (CCl_4, 15%): −2.5 ($2F_m$), −3.7 ($2F_m$)„ −14.6 ($2F_p$), −25.2 ($2F_o$), −27.4 ($2F_o$), −60.2 ppm (CF_2). Found: C 47.54, 47.28; H 1.17, 1.39; F 43.15, 42.95; N 5.37, 5.57%. $C_{21}H_6F_{12}N_2O$. Calculated: C 47.56; H 1.14; F 43.00; N 5.28%.

A solution of 1.6 g of compound (VI) in 3.4 ml of alcohol was refluxed for 6 min. The residue after removal of the solvent in vacuo was fractionally crystallized from petroleum ether to give 0.69 g (44%) of hydrazone (VII). From the mother liquor was isolated 0.3 g (19%) of compound (VIII), mp 112-113°. λ_{max} (heptane): 233 and 345 nm (log ε 4.2 and 4.08). F^{19} NMR (CCl_4, 11%): −1.4 ($4F_m$), −11.2 (F_p), −12.2 (F_p), −23.2 ($2F_o$), −24.8 ($2F_o$), −49.8 and 59.0 ppm (CF_2). Found: C 47.90, 47.92; H 1.29, 1.19; F 43.04, 43.29; N 5.47, 5.73%. $C_{21}H_6F_{12}N_2O$. Calculated: C 47.56; H 1.14; F 43.00; N 5.28%.

Reaction of Ketone (I) with Hydrazine (III). To a solution of 0.44 g of ketone (I) in 0.6 ml of alcohol was added in drops a solution of base (III) in 0.6 ml of alcohol. The solvent was removed in vacuo, and the residue was washed with absolute ether. We obtained 0.48 g (96%) of compound (IX), mp 108-110° (decompn.). λ_{max} (alcohol): 266 nm (log ε 3.27). Found: C 35.45, 35.42; H 1.78, 1.85; F 45.13, 45.13; N 11.39, 11.86%. $C_{15}H_8F_{12}N_4O_2$. Calculated: C 35.72; H 1.60; F 45.21; N 11.12%.

3,5-Bis-pentafluorophenyl-4,4-difluoro-5-hydroxypyrazoline (X). A solution of 0.5 g of compound (IX) in 1.5 ml of acetic acid was diluted with water. We obtained 0.43 g (95%) of pyrazoline (X), mp 110-111° (from petroleum ether). λ_{max} (alcohol): 284 nm (log ε 4.04). NMR (CCl_4, 11%): −3.98 and −7.34 ppm (OH and NH). F^{19} NMR (dioxane, 40%): −1.1 ($4F_m$), −10.6 ($2F_p$), −25.4 ($4F_o$), −41.2 and −58.0 ppm (CF_2, J_{FF} 266 Hz). Found: C 39.33, 39.36; H 0.52, 0.40; F 50.21, 50.43; N 6.08, 6.32%. $C_{15}H_2F_{12}N_2O$. Calculated: C 39.66; H 0.44; F 50.20; N 6.17%.

CONCLUSIONS

1. Perfluorodibenzoylmethane (I) reacts with hydrazine to form 3,5-bis-pentafluorophenyl-4,4-difluoro-5-hydroxypyrazoline (X).

2. Depending on the conditions, 1-phenyl-3,5-bis-pentafluorophenyl-4,4-difluoro-5-hydroxypyrazoline (VIII) and the monohydrazone of perfluorodibenzoylmethane (VII) are formed when ketone (I) reacts with phenylhydrazine.

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