REACTION OF NITRO- AND CHLORO-SUBSTITUTED PERFLUOROACETONES WITH N,N-DISUBSTITUTED HYDRAZINES

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Hydrazones of nitro- and chloro-substituted perfluoroacetones have not been described. Fokin et al. [1] have shown that nitropentafluoroacetone undergoes haloform cleavage under mild conditions upon the action of compounds containing NH₂ groups to give nitrodifluoromethane and trifluoroacetamide [1]. An exception was found only for benzamide, with which nitropentafluoroacetone forms an adduct [2]. Thus, attempts to obtain the hydrazone and semicarbazone of nitropentafluoroacetone by its reactions with 2,4-dinitrophenylhydrazine and semicarbazide naturally proved unsuccessful [1].

In the present work, we studied the reaction of nitropentafluoroacetone (I), chloropentafluoroacetone (II), and 1,2-dichlorotetrafluoroacetone (III) with N,N-disubstituted hydrazines in order to elucidate the possibility of obtaining the hydrazones of strongly electrophilic ketones.

The reaction of (I) with N,N-dimethylhydrazine and subsequent dehydration of the adduct (IV) by SoCl₂/pyridine* gave the dimethylhydrazone of nitropentafluoroacetone (V) [4].



 $X = NO_2$, Y = F(I); X = CI, Y = F(II); X = Y = CI(III); $X = NO_2$, Y = F, R = Me(V); $X = NO_2$, Y = F, R = Ph(IX); X = CI, Y = F, R = Ph(XI); X = Y = CI, R = Ph(XI).

Hydrazone (V) is not altered upon prolonged standing in ether or diglyme solution at about 20°C but decomposes upon an attempt to completely remove the solvent to give the dimethylhydrazone of trifluoropyruvul fluoride (VII).



We may propose the initial loss of an NO_2^- anion and its addition to intermediate olefin (VI) with subsequent loss of FNO.** The product structures were indicated by ¹H and ¹⁹F NMR spectroscopy and mass spectrometry as well as by the transformation of acid fluoride (VII) to methyl ester (VIII).

The lability of the nitro group in (V) is a consequence of +M effect of the dimethylamino group. Indeed, a stable hydrazone is obtained when one methyl group in hydrazone (V) is replaced by the electron-withdrawing phenyl group: (I) reacts with N-methyl-N-phenylhydrazine under analogous conditons to give the methylphenylhydrazone of nitropentafluoroacetone (IX) in about 70% yield. Similar procedures gave the methylphenylhydrazones of chloropentafluoroacetone (X) and 1,2-dichlorotetrafluoroacetone (XI). Hydrazones (IX)-(XI) are stable and were isolated by distillation in vacuum.

*The conditions for the dehydration of such adducts have been developed in our previous work [3]. **A radical mechanism for the decomposition of (V) as in the case of β -nitroperfluoroalkyl nitrites [5] is not excluded.

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Dimethylhydrazone of Nitropentafluoroacetone (V). A sample of 10.0 g (57 mmoles) (I) and 2.7 g (45 mmoles) N,N-dimethylhydrazine were added dropwise simultaneously to 200 ml abs. ether at -40°C and the homogeneous solution was maintained for 0.5 h at -10°C. The solution was recooled to -40°C and 7 g (88 mmoles) absolute pyridine and 6 g (50 mmoles) SOCl₂ were added dropwise simultaneously with stirring. The mixture was brought to about 20°C and the precipitate was removed. The ethereal solution was washed with water, dried over roasted MgSO₄, and 3/4 of the ether was removed in vacuum at about 20°C. The ¹H and ¹⁹F NMR spectra of the residue showed signals only for (V) and ether. IR spectrum (ν , cm⁻¹): 1360 and 1606 s (NO₂, C=N), 2900 m (CH). Mass spectrum: 235 M⁺, 189 (M⁺-NO₂), 159 (M⁺-NO₂, 2 Me), 139 (M⁺-CF₂NO₂). PMR spectrum (δ , ppm): 2.5 s (Me₂N). ¹⁹F NMR spectrum (δ , ppm): -27 m (CF₂), 3 m (CF₂), 3:2 ratio.

<u>Dimethylhydrazone of Trifluoropyruvyl Fluoride (VII)</u>. Distillation of the residue from the previous experiment gave 6.7 g (70%) (VII), bp 47°C (5 mm). IR spectrum (ν , cm⁻¹): 1540 and 1570 s (C=N), 1790 s (C=O), 2590 m (CH). Found: N 15.63%. Calculated for C₅H₆F₄N₂O: N, 15.05%. Mass spectrum: 186 (M⁺), 167 (M⁺-F), 139 (M⁺-COF), 117 (M⁺-CF₃), 58 (NNMe₂), 47 (COF), 44 (Me₂N). PMR spectrum (δ , ppm): 3.3 s (Me₂N). ¹⁹F NMR spectrum (δ , ppm): -107 q (COF), -15 d (CF₃), J_F/CF₃ 13 Hz, 3:1 ratio.

<u>Dimethylhydrazone of Methyl Trifluoropyruvate (VIII)</u>. A sample of 1.6 g (86 mmoled) and 4 ml absolute methanol were heated at reflux for 0.5 h. The mixture was diluted with water. The organic layer was separated, washed with water, dried over anhydrous MgSO₄, and distilled to give 1.2 g (70%) (VIII), bp 66-67°C (1 mm). IR spectrum (ν , cm⁻¹): 1570 (C = N), 1720 s (C = 0), 2920 and 2965 m (CH). Found: C, 36.20; H, 4.14; N, 14.36%. Calculated for C₆H₉F₃N₂O₂: C, 36.36; H, 4.55; N, 1414%. PMR spectrum (δ , ppm): 3.6 s (CH₃), 3.0 s N(CH₃)₂), 1:2 ratio. ¹⁹F NMR spectrum (δ , ppm: 3.6 s (N(CH₃)₂), 1:2 ratio. ¹⁹F NMR spectrum (δ , ppm): -14.6 (CF₃). Mass spectrum: 198 (M⁺), (M⁺-MeO), 139 (M⁺-MeOCO), 69 (CF₃).

<u>Methylphenylhydrazone of Nitropentafluoroacetone (IX).</u> A sample of 2.0 g (10 mmoles) (I) was added to a mixture of 1.1 g (10 mmoles) N-methyl-N-phenylhydrazine and 50 ml abs. diglyme at -60°C. The mixture was maintained at -30°C for 10 min and at 0°C for 10 min. The mixture was recooled to -60°C and 1.1 g SOCl₂ and 1.73 g abs.pyridine were added dropwise simultaneously with stirring. The mixture was diluted with water. The organic layer was separated, washed with water, and distilled in vacuum to give 1.9 g (62%) (IX), bp 107-109°C (15 mm). Found: C, 40.31; H 2.95; N 13.36%. Calculated for $C_{10}H_8F_5N_3O_2$: C, 40.40; H, 2.69; N, 14.14%. Mass spectrum: 297 (M⁺). PMR spectrum (δ , ppm): 7.0 (Ph), 3.4 s (Me), 5:3 ratio. ¹⁹F NMR spectrum (δ , ppm): -26 m (CF₃), 2.9 q. m (CF₂), 3:2.

Methylphenylhydrazone of Chloropentafluoroacetone (XI). By analogy, 6.8 g (37 mmoles) (II), 4.7 g (39 mmoles) N-methyl-N-phenylhydrazine, 4.65 g (39 mmoles) SOCl₂, and 6.4 g (81 mmoles) dry pyridine in 20 ml monoglyme gave 7 g (65%) (XI), bp 89-91°C (2 mm). Found: C, 42.61; H, 3.00; F, 30.06%. Calculated for $C_{10}H_8F_5ClN_2$: C, 41.90; H, 2.7; F, 30.30%. Mass spectrum: 286 (M⁺), 251 (M⁺-CF), 231 (M⁺-CF, Cl), 85 (CF₂Cl). PMR spectrum in CCl₄ (δ , ppm): 2.5 (Me), 6.4 (Ph), 3:5 ratio. ¹⁹F NMR spectrum (δ , ppm): of syn and anti isomers: -34.0 q (CF₂), -31 m (CF₂), -27 m (CF₃), -16.9 t (CF₃), 2:3 ratio.

CONCLUSIONS

1. Reactions of nitropentafluoroacetone, chloropentafluoroacetone, and 1,2-dichlorotetrafluoroacetone with N,N-disubstituted hydrazines gave the corresponding hydrazones for the first time. 2. The dimethylhydrazone in the absence of solvent is converted to the dimethylhydrazone of trifluoropyruvyl fluoride.

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REACTION OF ELEMENTAL PHOSPHORUS WITH PROPYLENE OXIDE IN THE PRESENCE OF TRIPHENYLPHOSPHINE AND PHENOL

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White phosphorus reacts with olefin α -oxides in the presence of protic compounds and amines, bases and alcoholates with the formation of phosphorus-containing polyols [1]. However, there is no information in the literature on the initiation of such reactions by P(III) derivatives having nucleophilic properties.

We are the first to show that white phosphorus reacts with propylene oxide and phenol in the presence of PP₃. The reaction products are phosphorus-containing polyols, which are lightly colored syrups highly soluble in alcohols, formamide, and DMSO. The IR spectra of the products show a broad vOH band at 3100-3500 cm⁻¹, vP-H band at 2280 cm⁻¹, vPhO band at 1260 cm⁻¹, and a broad vP=O band at 1200-1230 cm⁻¹. The ³¹P NMR spectra of the mixtures indicate that the reaction products contain phosphate, phosphonate, and phosphinate fragments. The peak with δP 21.5 ppm may be assigned to the phosphorus atom in phoshonium compound (I), which is one of the initially formed products.

 $\begin{array}{c} Ph_{3}P + CH_{3}CHCH_{2}O \xrightarrow{PhOH} Ph_{3}P^{\dagger}CH_{2}CHMeO^{-} \\ (II) & (I) \end{array}$

Product (I) probably attacks P4 as a strong nucleophilic, generating a phosphide anion, which leads to the formation of the reaction products.

The conversion of white phosphorus depends on the reaction conditions and is 7% for the system of 1:5:1:0.8 P₄:(II):PhOH:Ph₃P at 50-70°C over 7 h. The mixture was treated with methanol. Unreacted phosphorus was filtered off. The filtrate was evaporated. The residue was reprecipitated from methanol by the addition of ether and dried in vacuum. The system containing 5 g P₄, 11.7 g (II), 3.8 g PhOH, and 8.5 g Ph₃P gave 4.3 g product. Found: C, 66.98; H, 6.68; P, 10.52%.

CONCLUSIONS

Organophosphorus polyols may be obtained by the reaction of elemental phosphorus with propylene oxide initiated by trivalent phosphorus derivatives.

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