CYCLOADDITION OF NITRILE N-OXIDES TO BIS(TRIFLUOROMETHYL)KETENE

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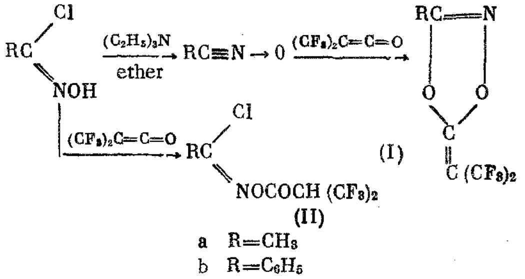
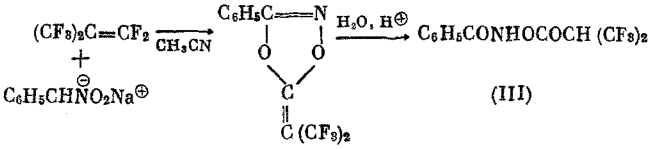
Nitrile N-oxides enter into a 1,3-dipolar cycloaddition reaction with various compounds containing multiple bonds [1]. In particular, it is known that the reaction of trimethylacetonitrile N-oxide with diphenylketene leads to 3-tert-butyl-4,4-diphenylisoxazol-5-one on account of the addition of the N-oxide to the ketene C=C bond [2,3]. The wider reaction of nitrile N-oxides with ketenes has evidently not been studied. Continuing a study of the reactions of nitrile N-oxides we have investigated the reaction of the N-oxides of acetonitrile and benzonitrile with bis(trifluoromethyl)ketene. As was shown in both cases, the main products are the appropriate 5-substituted 2-hexafluoroisopropylidene-1,3,4-dioxazoles (I) which are formed as a result of the cycloaddition of the N-oxides to the ketene C=O group.* Dependent on the conditions for carrying out the reaction more or less substantial quantities of the acid chlorides of the O-hexafluoroisobutyrylhydroxamic acids (II) are formed together with (I)



Structure (Ia) proved to be completely identical with the substance previously obtained by us from the reaction of perfluoroisobutylene with the sodium salt of nitroethane [5]. The dioxazole (Ib) is also obtained by an analogous reaction, this is converted into a derivative of the benzhydroxamic acid (III) by acid hydrolysis



The structure of the obtained substances is confirmed by the IR and NMR spectra.

EXPERIMENTAL

IR spectra were measured on a UR-10 instrument. NMR spectra were recorded on a Perkin-Elmer R-12 instrument with working frequency 60 MHz and internal standard HMDS. The F^{19} NMR spectra were

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* A number of cases are known in which cycloaddition to bis(trifluoromethyl)ketene is accomplished at the C=O and not the C=C bond [4].

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recorded on a Hitachi H-60 instrument with working frequency 56.46 MHz, chemical shifts were measured from CF_3COOH (external standard).

2-Hexafluoroisopropylidene-5-phenyl-1, 3, 4-dioxazole (Ib). To a solution of 8.7 g of the acid chloride of benzhydroxamic acid in 50 ml of absolute ether 5.7 g of triethylamine in ether was added with stirring at −10°C, 10 g of bis(trifluoromethyl)ketene was passed into the reaction mixture at −1° to −5° over 30 min, the mixture was stirred at −5° for 1 h, and left at 20° for 16 h. The precipitate of triethylamine hydrochloride was filtered off, fractionation of the filtrate in vacuum gave a fraction with bp 106-110° (2 mm) containing (Ib) and (IIb) (ν_{max} 1800 cm^{-1}), recrystallization of this fraction from petroleum ether yielded 11.4 g (68% of theory) of (Ib) with mp 52-54°. Found: C 44.74; H 1.82; F 38.62; N 4.75%. $C_{11}H_5F_6NO_2$. Calculated: C 44.4; H 1.68; F 38.38; N 4.71%. IR spectrum (ν_{max}, cm^{-1}): 1630 (C=N), 1710 (C=C); F^{19} NMR spectrum: −21.8 ppm (singlet).

To a suspension of 3 g of the Na-salt of phenylnitromethane in 30 ml of CH_3CN 14 g of perfluoroisobutylene was introduced with stirring and cooling to 0°. The mixture was slowly warmed to 20°, after 12 h the mixture of unreacted perfluoroisobutylene and $(CF_3)_3CH$ was distilled off by heating to 80°, the residue was evaporated in vacuum, CH_2Cl_2 was added, and the precipitate was filtered off. From the filtrate 1.5 g (20%) of (Ib) was isolated by distillation, this was identical with the sample obtained by the preceeding method.

To 1 g of the dioxazole (Ib) 1 g of concentrated H_2SO_4 was added with ice cooling. The mixture was warmed to 20° and poured onto ice. In the precipitate was obtained 0.65 g (61%) of O-hexafluoroisobutyrylbenzhydroxamic acid with mp 75-77° (from benzene). Found: C 42.09; H 2.21; F 35.30%. $C_{11}H_7F_6NO_3$. Calculated: C 41.90; H 2.22; F 36.19%. IR spectrum (ν_{max}, cm^{-1}): 1810 (COO), 1680 (CO), 3210 (NH). PMR spectrum (in CH_3CN): δ_{CH} 4.9 (heptet, J_{HF} 8 Hz), $\delta_{C_6H_5}$ 7.6 (multiplet), and δ_{NH} 10.8.

2-Hexafluoroisopropylidene-5-methyl-1, 3, 4-dioxazole (Ia) and the Acid Chloride of O-Hexafluoroisobutyrylacethydroxamic Acid (IIa). Under analogous conditions to the first experiment for preparing (Ib) 8.1 g of a mixture of (Ia) and (IIa) (3:1 according to GLC data) with bp 64-70° (15 mm) was obtained from 3.6 g of the acid chloride of acethydroxamic acid, 3.9 g of triethylamine, and 6.8 g of bis(trifluoromethyl)ketene in 80 ml of absolute ether. The substance (Ia) was identified in the mixture with an authentic sample by IR and NMR H^1 and F^{19} spectra. In order to isolate (IIb) 5 ml of concentrated H_2SO_4 was gradually added to 8.1 g of the mixture at −78°, the mixture was slowly warmed to 0°, poured onto ice, and extracted with ether. By fractional distillation 1.2 g of (IIb) was isolated with bp 79-80° (35 mm). The substance was further purified on a Varian Aerograph 1868-4 preparative chromatograph (column SE-30 on Chromosorb-W). Found: 26.32; H 1.59; F 42.35; N 5.27%. $C_6H_4F_6ClNO_2$. Calculated: C 26.51; H 1.47; F 41.98; N 5.15%. IR spectrum (ν_{max}, cm^{-1}): 1630 (C=N), 1800 (COO). PMR spectrum (in CCl_4) δ_{CH_3} 2.22 (singlet), δ_{CH} 4.0 (heptet, J_{HF} 7.5 Hz). F^{19} NMR spectrum: −13.7 (doublet, J_{HF} 7.5 Hz).

CONCLUSIONS

The cycloaddition of nitrile N-oxides to bis(trifluoromethyl)ketene leads to 2-hexafluoroisopropylidene-1, 3, 4-dioxazoles.

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