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Abstract

Full Text

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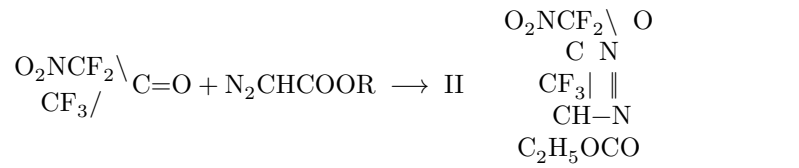
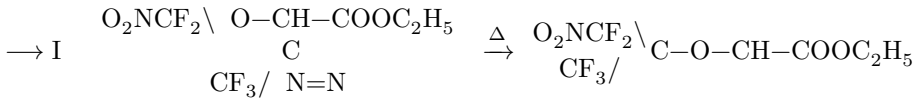
ON A CASE OF UNUSUAL ADDITION OF DIAZOACETIC ESTER TO KETONES

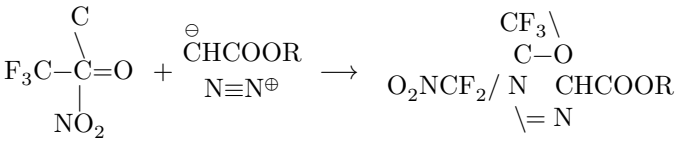
It is known that carbonyl compounds, including fluorinated ones, react with nucleophilic diazomethane to form α-oxides or homologous ketones. However, if electron-withdrawing substituents are present in the molecule of the diazo compound, its nucleophilicity is reduced to such an extent that it no longer enters into this reaction. Such diazo compounds react only at high temperature or in the presence of catalysts after elimination of nitrogen. In this case an electrophilic carbene is formed, which reacts not with the carbon but with the oxygen of the carbonyl group. Diazoacetic ester behaves similarly, giving with ketones the esters of the corresponding enols ([1,2]).

It might be expected, however, that with especially electrophilic ketones, a vivid representative of which is perfluoroacetone, diazoacetic ester, despite its decreased nucleophilicity, would react at carbon. Indeed, hexafluoroacetone reacts exothermically with diazoacetic ester to form β,β-bis-(trifluoromethyl)glycidic ester. Nitroperfluoroacetone, whose electrophilicity is still greater than that of perfluoroacetone, reacts vigorously with diazoacetic ester already at $-40°$; it is of interest that, in contrast to perfluoroacetone, a stable addition product is thereby formed, which only upon prolonged heating to 165° loses nitrogen and is converted into β-trifluoromethyl-β-nitrodifluoromethylglycidic ester. The adduct of nitroperfluoroacetone with diazoacetic ester, depending on the orientation of the addition, could have structure I or II. The reaction of the adduct with benzylamine, as a result of which it decomposes already at room temperature into difluoronitromethane, benzylamide of trifluoroacetic acid, and diazoacetic ester, is consistent only with the structure 2-carbethoxy-5-trifluoromethyl-5-nitrodifluoromethyl-Δ^3-1-oxadiazole-3,4 (I)

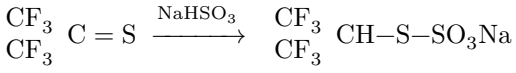


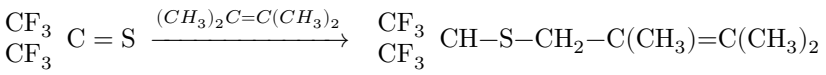


It might be supposed that the formation of I is explained by reverse polarization of the carbonyl group in nitroperfluoroacetone,

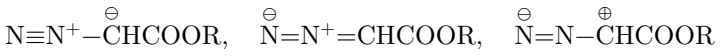


analogous reverse polarization of the thiocarbonyl group in thioperfluoroacetone (3)





However, the large difference in the electronegativity of carbon and oxygen makes this assumption unlikely. Consequently, the orientation of addition is determined by the electronic structure of the diazoacetic ester. Cases of addition of diazoacetic ester to multiple bonds without immediate elimination of nitrogen in this connection are of considerable interest, since they make it possible to establish the orientation of addition. The literature material on the products of addition of diazoacetic ester is scanty and contradictory (4-10). In some cases the formation of both isomers has been proved (11). Nevertheless, the principal structure of diazoacetic ester is generally taken to be structure (a)



(a) (b) (c)

and others.

Our results, however, which indicate nucleophilic attack on the carbonyl carbon by the terminal nitrogen atom, point to an appreciable contribution of structures of types (b) and (c).

Experimental Part

Ethyl β,β-bis-(trifluoromethyl)glycidate. Into 10 g of diazoacetic ester, while cooling with water, 9 ml of hexafluoroacetone was passed. This gave 17.6 g of a liquid with b.p. 74–75°/65 mm. Yield 82%. $n_D^{20} = 1.337$; $d_4^{20} = 1.417$. Found MR 36.8, calculated MR 36.597.

Found, %:	C 33.1, 33.11; H 2.37, 2.30; F 44.55, 44.27
$C_7H_6F_6O_3$. Calculated, %:	C 33.33; H 2.38; F 45.24

2-Carbethoxy-5-trifluoromethyl-5-nitrodifluoromethyl-Δ^3-1-oxadiazole-3,4 (I). To 8.2 g of nitroperfluoroacetone, 4.85 g of diazoacetic ester was added dropwise, with cooling to −40°. This gave 7.4 g (56.5%) of a liquid with b.p. 78–79°/8 mm; n_D^{20} 1.410, d_4^{20} 1.45. Found MR 46.3, calculated MR 47.05.

Found, %:	C 27.01, 27.22; H 2.17, 2.00; N 13.85, 13.58; F 30.05
$C_7H_6N_3F_5O_5$. Calculated, %:	C 27.3; H 1.96; N 13.7; F 30.9

To 3.1 g of oxadiazole I, 1.08 g of benzylamine was added gradually. After completion of the exothermic reaction, dinitrofluoromethane (identified by gas-liquid chromatography) and diazoacetic ester (b.p. 44–46°/12 mm, identified by conversion into the ester of N-phenylglycine, m.p. 58°) were isolated by distillation; in the residue, 1.3 g (88%) of trifluoroacetic acid benzylamide was obtained, with m.p. 70–71° (from petroleum ether), giving no depression of the melting point with an authentic sample.

Ethyl β-trifluoromethyl-β-nitrodifluoromethylglycidate. To 6.7 g of nitroperfluoroacetone, 4 g of diazoacetic ester was added dropwise and then heated at

165–170° until the evolution of nitrogen ceased. 3.3 g (35%) of a liquid was obtained, b.p. 46–47°/1 mm, n_D^{20} 1.3765, d_4^{20} 1.482. Found MR 43.2, calculated MR 42.597.

Found, %: C 39.51, 30.73; H 2.35, 2.37; N 5.07, 5.16; F 34.22, 34.34
$C_7H_6NF_5O_5$. Calculated, %: C 30.11; H 2.14; N 5.03; F 34.05

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Note: Figure translations are in progress. See original paper for figures.