SYNTHESIS OF 2,5-SUBSTITUTED 1,3,4-OXADIAZOLES

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A one-step method for the preparation of 2,5-dialkyl-1,3,4-oxadiazoles by condensation of aliphatic carboxylic acids and hydrazine hydrochlorides in the presence of phosphorus oxychloride is known [1]. The possibility of the application of this effective method for the preparation of 1,3,4-oxadiazoles with halogen atoms, nitro groups, or double bonds in the alkyl groups is not clear, inasmuch as one might expect that the appropriate aliphatic halo, nitro, or unsaturated carboxylic acids would undergo numerous side processes associated with chemical transformations of these groups on reaction with hydrazine hydrochloride and phosphorus oxychloride.

However, we have found that the sequence of reactions leading to oxadiazoles [1] proceeds quite rapidly in the case of the types of aliphatic acids enumerated above: side processes cannot compete appreciably with the formation of the oxadiazoles, and they are formed in good yields.

In the case of strong perhalogenated acids the reaction stops at the step involving the formation of diacylhydrazines, and it is necessary to add phosphorus pentachloride to the reaction mixture in order to bring about cyclization to oxadiazoles. The compositions and structures of the compounds obtained were confirmed unambiguously by the results of elementary analysis and the IR spectra, and the individuality of the substances was confirmed unambiguously by thin-layer chromatography (TLC).

EXPERIMENTAL METHOD

2,5-Bis(3,3,3-trinitropropyl)-1,3,4-oxadiazole. A mixture of 5.6 g (25 mmole) of γ,γ,γ-trinitrobutyric acid, 1.3 g (12.5 mmole) of hydrazine hydrochloride, and 25 ml of phosphorus oxychloride was heated at 85-95° for 20-24 h until all of the solids had dissolved. The excess phosphorus oxychloride was then removed by distillation, and the residue was treated with ice water. The resulting oil was extracted with chloroform, the solvent was removed, and the reaction product was recrystallized from alcohol to give a product with mp 88-89° in 54% yield.

The following compounds were obtained under similar conditions: 2,5-bis(3,3,3-fluorodinitropropyl)-1,3,4-oxadiazole (mp 70-72°, 69% yield), 2,5-bis(3,3,3-chlorodinitropropyl)-1,3,4-oxadiazole (mp 91-92°, 62% yield), 2,5-bis(3,3-dinitrobutyl)-1,3,4-oxadiazole (mp 76.5-78.5°, 66% yield), and 2,5-bis(β-styryl)-1,3,4-oxadiazole (the reaction temperature was 110-120°; mp 151-153°, 75% yield).

2,5-Bis(trichloromethyl)-1,3,4-oxadiazole. A mixture of 16.3 g (0.1 mole) of trichloroacetic acid, 5.25 g (0.05 mole) of hydrazine hydrochloride, and 50 ml of phosphorus oxychloride was heated at 110-120° for 24 h, after which 31 g (0.15 mole) of phosphorus pentachloride was added to the reaction mixture, and it was heated at 140° for another 10 h. The excess phosphorus oxychloride was removed by distillation, and the residue was vacuum distilled. The oxadiazole crystals obtained when the fraction with bp 105-110° (8 mm) was cooled were recrystallized from ether to give a product with mp 48° (mp 48° [2]) in 33% yield.

Diacylhydrazines, the melting points of which were in agreement with the literature values [3], were obtained under the same conditions but without the addition of phosphorus pentachloride. The results of elementary check analysis of the products corresponded to the following empirical formulas: N,N'-bis(trifluoroacetyl)hydrazine (mp 193°, 45% yield), N,N'-bis(heptafluorobutyryl)hydrazine (mp 161-162°, 50% yield), and N,N'-bis(perfluorooctanoyl)hydrazine (mp 138°, 47% yield).

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In contrast to 1,3,4-oxadiazoles, the IR spectra of the N,N'-diacylhydrazines contain characteristic absorption bands at 1700-1740 (C = O) and 3290-3300 cm^{-1} (N—H).

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