ELIMINATION OF CARBOXYL GROUP IN 3,8-DINITRO-6-OXO-6H-DIBENZO[b,d]PYRAN-10-CARBOXYLIC ACID BY THE ACTION OF DMSO OR DMFA

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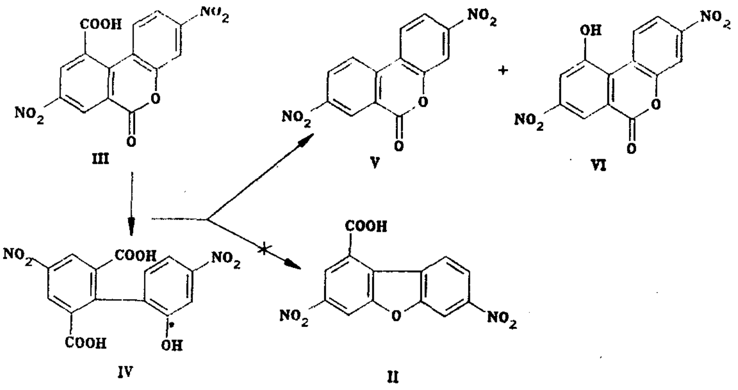
We have already shown that when heated in DMSO or DMFA, 3,8,10-trinitro-6H-dibenzo[b,d]-pyran-6-one (I) cyclizes to form 1-carboxy-3,7-dinitrodibenzofuran (II) [1].

In the course of examination of the properties of nitro-substituted 6H-dibenzo[b,d]pyran-6-ones, we studied the action of reactive, nondried DMSO and DMFA on 3,8-dinitro-6-oxo-6H-dibenzo[b,d]pyran-10-carboxylic acid (III), which contains substituents at the same positions as compound I. As in the case of compound I, in these solvents the lactonic bond of compound III is opened, and hydroxydicarboxylic acid IV is formed. However, when these solutions are boiled, there is no intramolecular cyclization with the formation of acid II. 3,8-Dinitro-6H-dibenzo[b,d]pyran-6-one (V) and 3,8-dinitro-10-hydroxy-6H-dibenzo[b,d]-pyran-6-one (VI) were isolated from the reaction mixture [VI, mp 291.5-292.5°C (dec) (from acetic acid); R_f 0.5 (7:1 benzene–acetone mixture, Silufol UV-254 plates) IR spectrum (KBr): 3300-2900 (OH), 1730 (C=O), 1525 and 1350 cm^{-1} (NO_2). The compound has satisfactory analytical characteristics]. Thus a decarboxylation reaction and exchange of the carboxylic group for a hydroxy group take place, possibly because of water present in the solvent. It is interesting to note that a similar reaction did not occur in the case of compound II or the structurally similar 4-carboxy-2,7-dinitrofluorenone, containing dibenzofuran and fluorene rings that are stable toward cleavage in DMSO and DMFA. We can thus assume that in the above transformations of compound III, its open form participates in the reaction.



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