SYNTHESIS OF 6-HALO-4,7-DIHYDRO-7-OXO-1,2,4-TRIAZOLO[5,1-c][1,2,4]TRIAZINES BY REPLACEMENT OF THE NITRO GROUP

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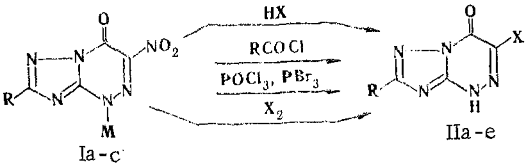
Replacement of the nitro group in aromatic and heteroaromatic rings by halogens is a phenomenon that is quite rare and is of considerable synthetic interest [1].

The possibility of replacing the nitro group in a series of 6-nitro-7-oxo-4,7-dihydro-1,2,4-triazolo[5,1-c][1,2,4]triazine derivatives by the action of hydrogen halide in alcohol (method A) [2] opened up a pathway to the synthesis of various previously inaccessible halo derivatives, the yields of which were ∿90%. A similar reaction takes place in the interaction of Ia-c with acyl halides (method B; the products are obtained in 65-80% yields) and, most simply and conveniently, with phosphoric acid chlorides ($POCl_3$, PCl_3, and PBr_3) (method C; the yields are 90-95% for IIa-c and 60-65% for IId,e). It is most likely that in these cases replacement of the nitro group proceeds as nucleophilic substitution with participation of Cl^-.



I M=Na, K; a R=H; b R=CH_3; c R=C_6H_5; II a R=H, X=Cl; b R=CH_3, X=Cl; c R=C_6H_5, X=Cl; d R=H, X=Br; e R=C_6H_5, X=Br

When Ia (M = H) was refluxed in benzene with KCl and 18-crown-6, despite the very low solubility of KCl in this system, we were, nevertheless, able to record the formation of chloride IIa by thin-layer chromatography (TLC). In addition to the data in [2], this serves as an argument in favor of the nucleophilic character of the replacement of the nitro group in the reactions described.

We have found that replacement of the nitro group by halogen occurs not only in the reaction of salts Ia-c with nucleophilic reagents (methods A-C) but also unexpectedly under conditions in which electrophilic halogenation usually takes place, viz., in the reaction with chlorine at 20°C and with bromine at 50-80°C in acetic acid (method D; the yields were 80-90% for the chlorides and 45-55% for the bromides). The data from the IR, UV, and PMR spectra of the compounds obtained were in agreement with structure II, and the results of elementary analysis were in agreement with the calculated values.

LITERATURE CITED

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