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NITRATION OF 2-CHLOROTROPONE. VARIOUS TYPES OF REARRANGEMENT OF 2-CHLORO-7-NITROTROPONE

T. Nozoe, T. Mukai and K. Sakai,
Department of Chemistry, Faculty of Science,
Tohoku University,
Sendai, Japan.

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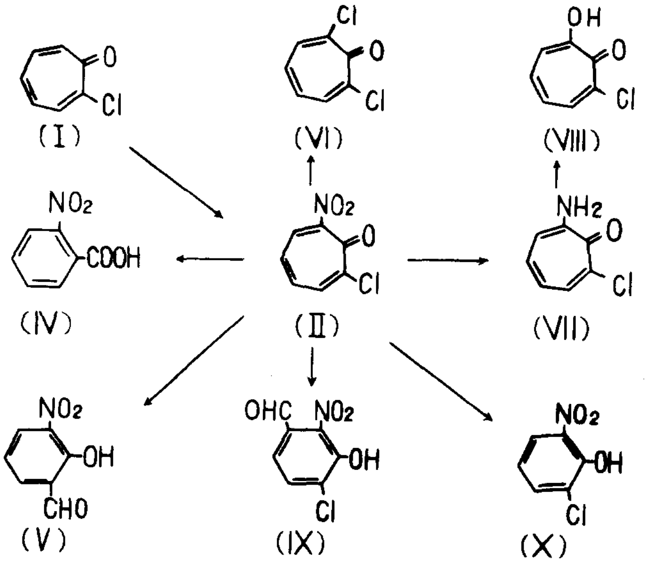
Nucleophilic reactions of troponoid compounds often result in rearrangements to give benzenoid compounds besides displacement reactions.[1] These rearrangements, in general, afford derivatives of benzoic acid and salicylaldehyde[2] or their functional derivatives. It has been reported that benzoic acid derivatives resulted from the rearrangement in which the C_1 carbon atom in the tropone ring was extruded during nucleophilic attack[3] and that salicylaldehyde derivatives were formed from the rearrangement when the C_3 carbon atom was extruded.[4] Furthermore, from the fact that the reaction of 5-bromo- or 5-iodo-2-methoxytropone with liquid ammonia gave vanillin, though in very poor yield,[5] it seems likely that extrusion of the C_4 carbon atom can also occur during contraction of the tropone ring.[4]

Recently, we found that 2-chloro-7-nitrotropone (II), prepared from 2-chlorotropone (I), on being treated with aqueous acetic acid or a mixture of water and ethanol, easily rearranged with extrusion of the C_5 or C_6 (C_4 or C_3) carbon atom from the tropone ring.[6] The recent publication of Forbes and Warrell,[7] describing a similar type of rearrangement, prompts us to report an outline of our findings.

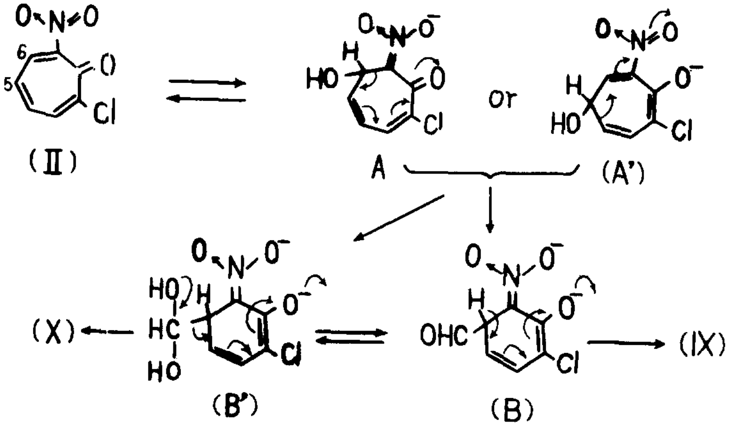
Treatment of I with fuming nitric acid in acetic acid at room temperature afforded a neutral substance (II), $C_7H_4O_3NCl$,[8] m. p. 118°, and an acidic substance $C_7H_3O_6N_2Cl$ (III), m. p. 109°, (30 and 10% yield respectively). The spectral data of II are as follows: IR in KBr; 1634, 1585 (C=C, C=O), 1536, 1362 cm^{-1} (NO_2). UV maxima in ethanol; 241 and 325 mμ (log ε 4. 08 and 3. 43). Under ice-cooling, II gave o-nitrobenzoic acid (IV) (60% yield) by treatment with 0. 5 N sodium hydroxide, and with sodium methoxide in methanol it gave a mixture of IV, the methyl ester of IV, and 3-nitrosalicylaldehyde[9] (V) (11, 25 and 35% respectively). When II was heated with hydrogen chloride in acetic acid in a sealed tube at 60-70°, it afforded 2,7-dichlorotropone[10] (VI), quantitatively. Since catalytic reduction of II gave 2-amino-7-chlorotropone (VII), m. p. 143°, which could be hydrolyzed to 3-chlorotropolone[11] (VIII), the correctness of structure of II is confirmed.

When II was heated in aqueous acetic acid on a boiling water bath, it afforded 4-chloro-3-hydroxy-2-nitrobenzaldehyde[12] (IX) (40%), whereas when II was heated in aqueous ethanol (1:1), (without addition of acid or base) it readily underwent a rearrangement to yield 2-chloro-6-nitrophenol[13] (X) (ca. 5%) as well as IX (30%). In this reaction, the formation of formic acid was proved by a mercuric chloride test.

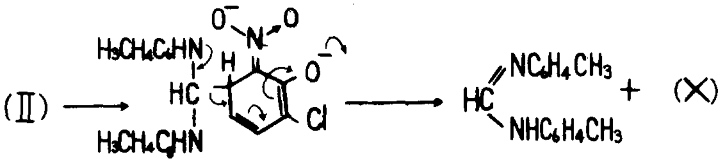


In this laboratory, it has been found that 4-alkyl- or 4-phenyl-5,7-dinitrotropolone and 3,5,7-trinitrotropolone, on being warmed in an aqueous solvent at 50-60°, afforded the corresponding nitrobenzoic acid derivatives in a good yield.[14] In this series of reactions, extrusion of the C_1 carbon atom of the tropolone ring is thought to have occurred during the ring contraction. However, in the formation of IX and X from II, the carbon atom at the C_5 or C_6 position must have been extruded. The pathway to IX and X can be explained as depicted in the following scheme.

The non-occurrence of a nucleophilic attack at the C_1 position of II is attributed to the steric interference by the substituents at the C_2 and



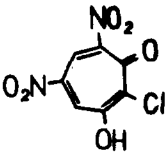
C_7 positions. Moreover, a combination of the polarizing and inductive effects of the nitro, carbonyl, and chloro groups would aid attack by a water molecule at the C_5 or C_6 position and the subsequent ring contraction (shown by A or A$'$ to B or B$'$). The lone-pair electrons on the oxygen atom at the C_1 position of the intermediate (B or B$'$) would be abstracted by the nitro group of II,[15] and this would lead to the elimination of either a proton or formic acid, giving thus IX or X. The fact that X was obtained from the reaction in aqueous ethanol can be attributed to the elimination of formic acid through the intermediate (B$'$). In view of the different products resulting from the treatment of II with strong bases, water, and acids, it would be of interest to examine the effect on II of weak bases such as aryl amines. Treatment of II with p-toluidine in benzene or ethanol at room temperature afforded X (13%) and N,N$'$-di(p-tolyl)formamidine[16] (XI) as its hydrochloride (20%). In this reaction, the intermediate (C), derived by attack of p-toluidine to II, eliminated XI under oxidizing conditions and gave X, as depicted below.



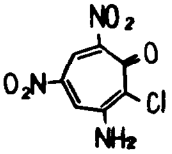
(C)

(XI)

The acidic substance (III) was shown to be 2-chloro-5,7-dinitro-3-hydroxytropone from the following spectral data. IR in KBr; 3115 (OH), 1613, 1570 (C=C, C=O), 1550, 1348 cm^{-1} (NO_2). UV maximum in cyclohexane; 367 mμ (log ε 4.19). NMR spectrum (in $CDCl_3$); -1.50 τ (OH proton), 1.01 and 1.40 τ with J=2.5 cps (two aromatic protons at 1,3 positions). Unlike the α-tropolones, III did not give a color test with ferric chloride. Also, when III or its methyl ether was heated with potassium hydroxide, no rearrangement resulted and in each case III was recovered. Reaction of the methyl ether with ammonia afforded an amino compound (XV), m.p. 152.5°, which, on being treated with dilute sodium hydroxide solution, regenerated III.



(III)



(XV)

The experimental details of this study and several related rearrangements will be published in the near future.

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