

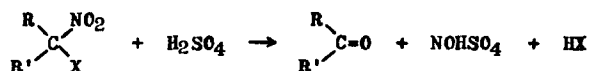
A NEW REACTION OF α -HALONITROALKANES

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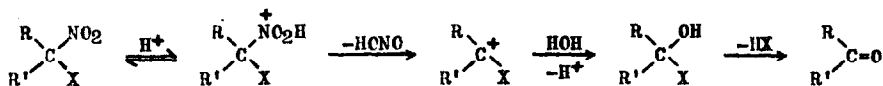
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We wish to report a new reaction of α -halonitroalkanes together with a mechanistic interpretation. We have found that α -bromo and α -chloro derivatives of secondary nitroalkanes react with strong acid to furnish ketones. For example, 2-bromo-2-nitropropane and concentrated sulfuric acid combine exothermally and produce an opaque mixture in which nitrosylsulfuric acid was detected by the Liebermann test.² Acetone was isolated in 60% yield as its 2,4-dinitrophenylhydrazone from the steam distillate of the diluted reaction mixture. 1-Bromo-1-nitrocyclohexane and its chlorine analog react similarly with sulfuric acid to furnish cyclohexanone; 2-chloro- and 2-bromo-3,3-dimethyl-2-nitrobutane produce pinacolone.

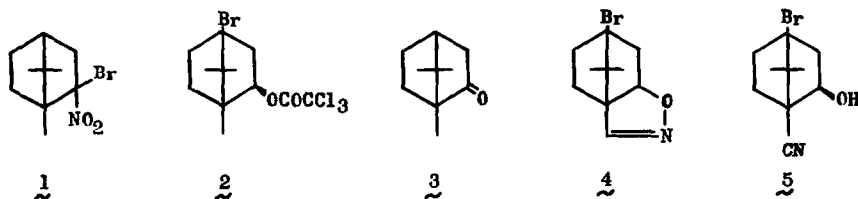


With the bromonitroalkanes as starting materials, α -brominated ketones arise as by-products from secondary reactions between the ketone and elemental bromine, the halogen resulting from oxidation of hydrogen bromide by the sulfuric acid medium.

A plausible mechanism for the transformation incorporates an earlier speculation³ and a recent observation⁴ that acid cleaves the nitro group from these substances to form a carbenium ion. Strong acid reversibly protonates the nitro group.⁵ Generation of a carbonium ion accompanies separation of the protonated nitro group as nitrous acid which is then transformed into nitrosylsulfuric acid⁶ by the medium. Reaction of the cation with water and a subsequent elimination (or an equivalent sequence) furnish the ketone.



The behavior of dl-2-bromo-2-nitrobornane⁷ (1) in strong acid supports several features of the proposed mechanism. When heated in trichloroacetic acid, 1 affords 4-bromo-exo-2-bornyl trichloroacetate (2) plus camphor (3), 6-bromo-5,6,7,7a-tetrahydro-8,8-dimethyl-4H-3a,6-methano-1,2-benzisoxazole³ (4), and 4-bromo-exo-2-hydroxy-7,7-dimethyl-1-norbornanecarbonitrile³ (5). The trichloroacetate was identified by saponifi-



cation to 4-bromo-exo-2-bornanol.⁸ The retention of bromine and, importantly, the absence of any nitrogen-containing group in the ester clearly show that the carbon-nitrogen bond undergoes cleavage before fracture of the carbon-halogen bond. Moreover, the extensive rearrangement of the terpenoid skeleton in the transformation of 1 into 2 attests to the cationic nature of a subsequent intermediate. Skeletal rearrangements suppress the formation of camphor from 1.

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