Reactions of a Stable Nitronic Ester

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THE instability of nitronic esters has been a barrier to studies of their reactions.[1] Recently reported novel transformations[2,3] of nitro-compounds prompt our report on the preparation and reactions of a stable nitronic ester.

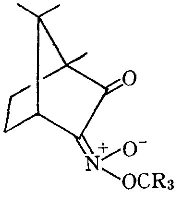
The sodium salt of 3-nitrocamphor and triphenylmethyl chloride gave trityl camphor-3-nitronate (I), 44%, m.p. 149—152°, $[\alpha]_D + 108°$ (benzene). The infrared spectrum had a band at $5\cdot80\mu$, indicative of an $\alpha\beta$-unsaturated carbonyl group.[4] The infrared spectrum of 3-nitrocamphor showed absorption due to the carbonyl group at $5\cdot65\ \mu$.[5] The ultraviolet spectrum with λ_{max} (ether) 288 mμ (ϵ, 13,900) was similar to the nitrone [(II), λ_{max} (ethanol) 280 mμ (ϵ, 17,500)].[6]

Treatment of the nitronic ester (I) with dilute alcoholic sodium hydroxide gave triphenylcarbinol (88%) and 3-nitrocamphor (56%). Hydrogenolysis of the nitronic ester occurred with platinum and hydrogen to form triphenylcarbinol (86%) and a mixture of amino-alcohols which gave an infrared spectrum similar to the spectrum of β-aminoborneol. The above data are consistent with (I) for the structure of the product and exclude both the enol ether of 3-nitrocamphor and the product of alkylation at C-3.

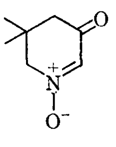
The nitronic ester reacted with piperidine to form triphenylcarbinol (35%) and the hydroxamic acid (III), 37%, m.p. 161—162°, which showed characteristic bands in the infrared spectrum at $3\cdot00$—$4\cdot20$ and $6\cdot00\mu$. Presumably, the intermediate nitrile oxide was hydrolyzed. The nitronic ester reacted similarly with pyrrolidine.

The nitronic ester isomerized at 125° in xylene. The product [λ_{max} (ether) 268 (ϵ, 1960) and 275 mμ (ϵ, 1320)] was isolated in a yield of 33%, m.p. 176—177°, $[\alpha]_D + 78°$ (benzene). The infrared spectrum had a band at $5\cdot71\ \mu$ characteristic of the carbonyl group in camphor.[4] A signal in the n.m.r. (60 Mc./sec.) spectrum at δ 3·44 (doublet, 1 H) identified the bridgehead proton. The spectral data indicated that the product of thermal isomerization was the saturated ketone (IV).

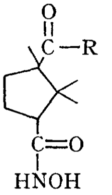
In the presence of pyridine, the oxaziran (IV) was converted into the semicarbazone (V), m.p. 197—198°, clearly demonstrating the presence of a carbonyl group. The oxaziran was reduced with hydrogen and platinum to the alcohol (VI), m.p. 184—185°. Subsequent reductions with hydrogen and platinum and also with sodium borohydride gave mixtures of epimeric alcohols which had infrared spectra identical to the spectrum of (VI). The unusual stability[7] of (IV) must be due to the inclusion of the oxaziran ring within a rigid bicyclic system and to the protection provided by the bulky triphenylmethyl group. Steric effects also accounted for the remarkable stability of the oxiran ring in picrotoxinin.[8]



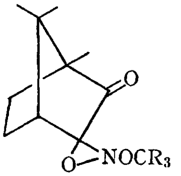
(I) R = Ph



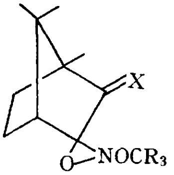
(II)



(III) R = $C_5H_{10}N$

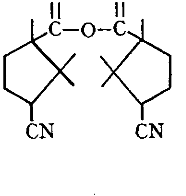


(IV) R = Ph



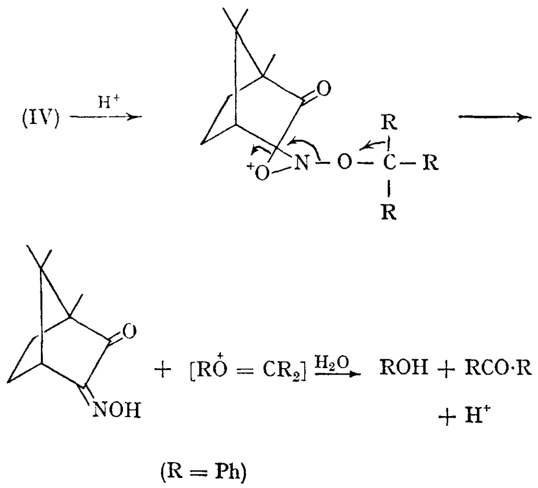
(V) R = Ph; X = NNH·CO·NH$_2$
(VI) R = Ph; X = H,OH

The oxaziran (IV) was treated with acid according to a procedure by Emmons[9] for the hydrolysis of oxazirans.[7] Isonitrosocamphor (87%), benzophenone (86%), and phenol (50%), identified as its tribromo-derivative, were isolated.



(VII)

Isolation of isonitrosocamphor demonstrated that the nitronic ester (I) was converted into the oxaziran (IV) without skeletal rearrangement. The acid-catalyzed hydrolysis of the oxaziran (IV) in aqueous methanol appears to be a heterolytic



process in which a phenyl group migrates to an electron-deficient oxygen atom forming a fragment which is hydrolyzed to phenol and benzophenone.

The extremely low solubility of (IV) in water precluded some of the tests for oxazirans.[7] Pyrolysis of the oxaziran at 280° yielded a compound with physical properties in agreement with those reported for the anhydride (VII).[10] Bands in the infrared spectrum were present at 4·48 (nitrile), 5·58, and 5·77μ (anhydride).

The synthesis of an oxaziran from a stable nitronic ester supports the concept that some reactions of primary and secondary nitro-compounds may be interpreted on the basis of oxaziran intermediates.[11] An oxaziran intermediate may be involved in the rearrangement[12] of α-nitro-ketones to *N*-hydroxy-imides.[13]

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[13] Satisfactory analyses were obtained for all new compounds. Readily available known compounds were compared with authentic samples and identified by infrared analysis (KBr).