The Thermal Decomposition of 2-Azidotropone

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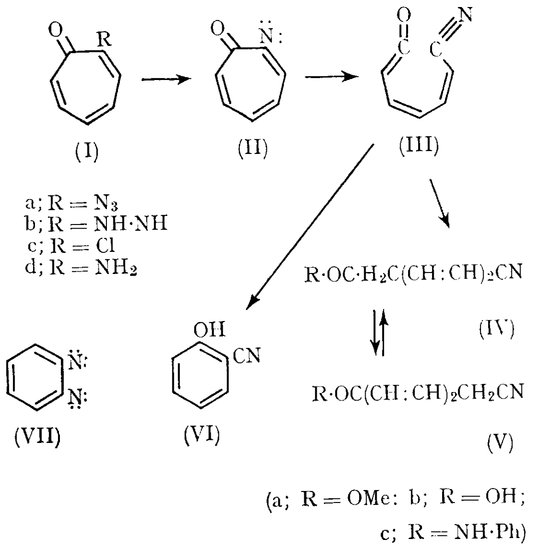
THE interesting reactivity displayed by certain aromatic nitrenes[1,2] led us to examine the behaviour of such species in non-benzenoid aromatic systems, and we report here some preliminary observations on derivatives of tropone.

2-Azidotropone (Ia) was obtained as unstable yellow crystals, m.p. 28°, either by treatment of the 2-hydrazino-derivative (Ib) with nitrous acid, or from 2-chlorotropone (Ic) by reaction with sodium azide in dimethyl sulphoxide at 15°. A solution of the azide in refluxing cyclohexane rapidly evolved nitrogen, decomposition being complete after 15 minutes; the major product, *o*-salicylonitrile (VI), was generally formed in yields of greater than 90%, but was accompanied by traces of ketonic material, so far unidentified. The phenol was also the sole product isolated from photolysis of an ethereal solution of the azide at room temperature, but only intractable tar was obtained by direct oxidation of a benzene solution of 2-aminotropone (Id) with lead tetra-acetate.[2b]

No phenolic material was detectable in the products resulting from the decomposition of the azide in protic solvents. In the presence of water, aniline, or methanol, the unsaturated acid or its derivatives (IV), evidently resulting from addition to an intermediate keten (III), were formed, although isolation and identification was complicated by concurrent geometric and prototropic rearrangements. Thus, thermolysis of the azide (Ia) in boiling methanol afforded a conjugated nitrile (IVa), m.p. 62°, ν_{max} $(CCl)_4$ 2215, 1745 cm.$^{-1}$, λ_{max} (EtOH) 254 mμ (ϵ, 24,500), together with lesser amounts of a conjugated ester (Va), m.p. 72°, ν_{max} (CCl_4) 2250, 1723 cm.$^{-1}$, λ_{max} (EtOH) 250 mμ (ϵ, 23,100), the proportion of which increased with longer reaction time to a maximum of about 25%. Structural confirmation was provided by hydrolysis and reduction of the higher-melting isomer to pimelic acid; either pure isomer was converted into the equilibrium mixture by prolonged boiling in methanol. The n.m.r. spectrum of the mixed



esters resulting from decomposition of the azide in $[^2H_1]$methanol lacked the signals characteristic of the two allylic and one olefinic protons, indicating that interconversion proceeds *via* prototropic exchange with the solvent rather than by intramolecular 1,5-hydrogen transfer. The esters therefore probably have all-*trans*-geometry.

Decomposition of the azide in aqueous dioxan or aniline similarly gave mixtures from which a corresponding acid (IVb) and an anilide (IVc) have been isolated. The keten (III) presumably originates from the nitrene (II) by a ring fission akin to that recently observed in the case of the dinitrene (VII),[2] and the formation of *o*-salicylonitrile in the aprotic solvent can be ascribed to a valence isomerisation of the hexatriene–cyclohexadiene type. A closely analogous cyclisation is considered to account for the presence of *o*-vinylphenol among the thermolysis products of cyclo-octa-1,3,5-trien-7-one.[3]

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