Monosubstituted Cyclopropenones from Terminal Acetylenes

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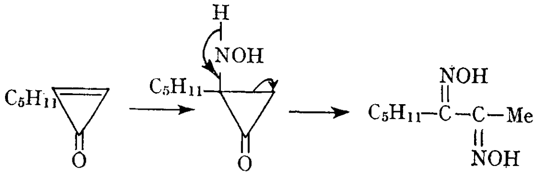
DISUBSTITUTED cyclopropenones are now a well-established class[1] and evidence for a ring current in the system has been deduced from the observed deshielding of the α- and β-methylene protons in aliphatic substituents and of the *ortho*-protons in aromatic substituents. Hitherto, however, neither cyclopropenone itself nor monosubstituted cyclopropenones have been available in order to examine the degree of the deshielding of a proton attached directly to the ring.

We now report a route of some generality to the latter type of compound. Thus oct-1-yne was converted by hypobromous acid[2] into 1,1-dibromooctan-2-one, treatment of which with triethylamine in acetonitrile at 55° gave pure n-pentylcyclopropenone reproducibly in 10—15% yield; purification involved extraction into hydrochloric acid and short-path distillation. The infrared spectrum (liquid film) showed strong bands at 1830 and 1590 cm.$^{-1}$ Only end-absorption was shown in the ultraviolet spectrum. The n.m.r. spectrum ($CDCl_3$) showed a sharp singlet assigned to the ring proton at τ 1·53 (1H), a triplet at τ 7·3 (2H; J = 7 c./sec.), a triplet of triplets centred at τ 8·25 (2H; $J_1 = J_2 =$ 7 c./sec.), a multiplet at τ 8·53 (4H), and a triplet at τ 9·08 (3H; J = 6 c./sec.). Of these resonances only those due to protons in the immediate environment of the ring showed appreciable shifts in CF_3CO_2H/CCl_4, the α-methylene protons appearing as a triplet at τ 7·17 and the ring proton as a singlet at τ 1·32; the fact that these shifts are small reflects the high degree of polarisation of the cyclopropenone system even in $CDCl_3$. Catalytic hydrogenation (Pd–C) gave n-hexyl methyl ketone as the main product. Reaction with hydroxylamine produced a novel and unexpected result with the formation in good yield of the highly crystalline n-pentylmethylgloxime, m.p. 170—171°[3] (structure confirmed by n.m.r. and mass spectrometry). A tentative mechanism for this ring fission can be envisaged as shown in the flowsheet. The smoothness of this cleavage renders it a useful characterising reaction for alkylcyclopropenones.

A similar procedure led to the production of the far more labile ethylcyclopropenone which rapidly darkened on standing. Attempts to prepare cyclopropenone itself by this method have so far proved fruitless. As expected, application of the process to symmetrical dialkylacetylenes furnished the corresponding unsymmetrical dialkylcyclopropenones, which gave the expected mixtures of two isomeric glyoximes by the hydroxylamine fission.



(*Received, January 25th,* 1966; *Com.* 049.)

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