The Reaction of Acetylenes with Bicyclopentane

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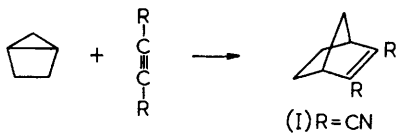
ALTHOUGH the chemistry of cyclopropane and its derivatives has been vigorously explored during the past decade, relatively little is known about the effect of added strain on the reactivity of the cyclopropyl ring. We now report what we believe to be the first example of the reaction of a strained cyclopropane with substituted acetylenes.

When bicyclo[2,1,0]pentane was allowed to stand at room temperature for five days with dicyanoacetylene, a mixture of two products was obtained in 53% yield. Chromatography of this mixture on activity grade III neutral alumina afforded 2,3-dicyanobicyclo[2,2,1]hept-2-ene (I), m.p. 42·0—42·8° (lit.[1] m.p. 42·5°), λ_{max} (ethanol) 249 mμ (ϵ 9,900). The infrared spectrum and nuclear magnetic resonance spectrum of (I) were



(I) R = CN
(II) R = CO_2Me

identical with those of an authentic sample. A mixed melting point was undepressed.

A similar reaction was observed between bicyclo[2,1,0]pentane and dimethyl acetylenedicarboxylate. However, in this case the reaction required five days at 100° in a sealed tube under nitrogen. Distillation gave a 70% yield of material, b.p. 120—125°/4·7 mm. Again the reaction product consisted of two components. Preparative vapour-phase chromatography on a 15-foot × $\frac{3}{8}$-inch column packed with 20% butanediol succinate on 42/60 Chromosorb-P provided a simple means of separating the two products. The initially eluted component, λ_{max} (ethanol) 236 mμ (ϵ 8,400), $n_D^{24.5°}$ 1·4878, was identified as dimethyl bicyclo[2,2,1]hept-2-ene-2,3-dicarboxylate (II) by comparison with an authentic sample (lit.[2] b.p. 132—133°/12 mm.).

Bicyclo[2,1,0]pentane gave no reaction with diphenylacetylene. Combined with the fact that dicyanoacetylene reacted much faster than dimethyl acetylenedicarboxylate, this indicates that an electron-deficient acetylene is required in order for the addition to occur. The failure of dimethyl acetylenedicarboxylate to react with bicyclo[3,1,0]hexane under conditions suitable for cycloaddition to bicyclo[2,1,0]pentane demonstrated the dependence on ring strain.

Work is continuing on elucidating the structure of the second component obtained in these reactions.

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