Photorearrangements of 1-Cyanocyclohexenes. A "Type A" Process Involving the Acrylonitrile Chromophore

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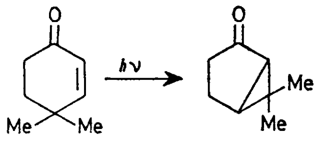
Summary Irradiation of simple 1-cyanocyclohexenes gives derivatives of cyanobicyclo[3.1.0]hexanes, for which structural evidence is presented.

The di-π-methane rearrangement[1] has been extensively studied from the viewpoints of structural dependence, stereochemistry, and mechanism. In contrast, photorearrangements of the σ molecular framework have been less widely studied, the best known case being the 'type A' arrangement (*e.g.* **1** → **2**) of α,β-unsaturated ketones.[2] The latter reaction has been the subject of kinetic[3] and stereochemical[4] studies.

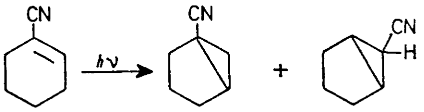


(1) (2)

We now report a photorearrangement of 1-cyanocyclohexene which formally resembles the 'type A' rearrangement[3] of enones.

Irradiation of 1-cyanocyclohexene (**3**), in purified hexane, with the full arc of a Hanovia type L 450W lamp in a water-cooled quartz immersion well gave 1-cyanobicyclo[3.1.0]hexane (**4**), and the *exo* and *endo* isomers of 6-cyanobicyclo[3.1.0]hexane (**5**). The products (**4**) and (**5**) were formed in equal amounts.

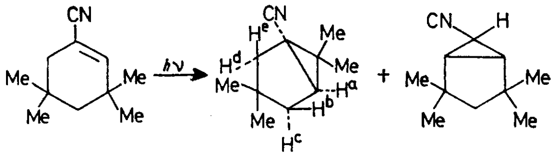
These products were isolated by preparative g.l.c.,† and their structures were proved by synthesis. Product (**4**) was prepared from 1-cyanocyclopentane by treatment with dimethylsulphoxonium methylide[5] in dimethyl sulphoxide.



(3) (4) (5)

Reaction of cyclopentene with cyanocarbene[6] (CNCH:) gave the epimers of (**5**). The synthetic materials and photolysis products had identical n.m.r. spectra, and g.l.c. behaviour. Both the compounds were hydrogenolysed, using 10% Pd/C in 95% ethanol at 25 lb in^{-2} and room temperature, to afford cyanocyclohexane.

Irradiation of 1-cyano-3,3,5,5-tetramethylcyclohexene (**6**), which can be synthesized readily from isophorone, gave products identified as the bicyclohexanes (**7**) and (**8**) in a ratio of 80:20, respectively. These compounds were isolated and purified by column chromatography and g.l.c. The i.r. spectra showed an unconjugated nitrile band at 2230 cm^{-1}. The structures were assigned from the 220



(6) (7) (8)

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† Preparative g.l.c. was performed on 5′ × ¼″ of 7% QF-1 on 60-70 mesh Chromosorb W with helium at 90 ml/min. (**4**) and (**5**) were resolved at 80 °C, and (**7**) and (**8**) at 120 °C.

MHz proton n.m.r. spectra. The spectrum of (**8**) is simple owing to the symmetry of the molecule: δ 0·87 and 1·28 (each 2H, d, J 14·0 Hz, ring CH_2), 1·01 [1H, t, J 3·5 Hz, $>$C(CN)H, partially obscured by Me signal], 1·02 and 1·21 (each 6H, s, Me), and 1·77 (2H, α, bridgehead CH).

The ^1H n.m.r. spectrum of (**7**) showed resonances at δ 0·98, 1·06, 1·17, and 1·31 (all 3H, s, Me), 1·18 (1H, dd, $J_{a,b}$ 7, $J_{b,c}$ 4·0 Hz, H^b, partially obscured by Me signal), 1·51 (1H, d, $J_{d,e}$ 14 Hz, H^e), 1·63 (1H, m, H^a), 1·77 (1H, dd, $J_{a,e}$ 2, $J_{d,e}$ 14 Hz), and 1·93 (1H, dd, $J_{a,c}$ 13·0, $J_{b,c}$ 4·0 Hz, H^c). The value of 2 Hz for $J_{a,e}$ is reasonable for **W** coupling[7] between H^a and H^e. The ^{13}C-n.m.r. spectrum was also consistent with the assigned structure.

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