The Addition of Dicyanoacetylene to Tricyclo[4,1,0,0^{3,7}]heptane

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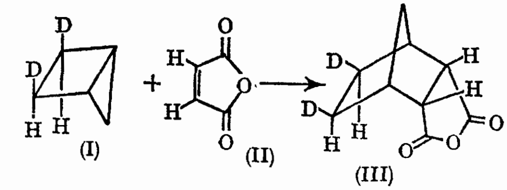
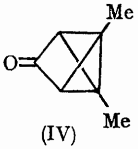
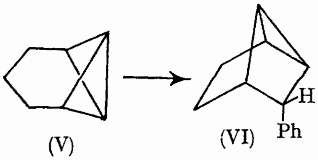
RECENTLY, we reported that the addition of electron-deficient carbon–carbon multiple bonds to highly strained carbon–carbon single bonds[1] occurs *via* rear attack on the "bent" carbon–carbon σ-bond as illustrated by the reaction of (I) with (II) to yield (III).[2] Subsequent to our work, Pomerantz and his co-workers attributed the failure of (IV) to react with benzyne to this requirement of rear attack.[3] In contrast to the findings of Pomerantz we have shown that (V) reacts with benzyne to give (VI) in 61% yield, thus establishing that severe steric hindrance [by the trimethylene bridge of (V)] is incapable of stopping the addition of carbon–carbon multiple bonds to strained σ-bonds.[4]



(I) (II) (III)



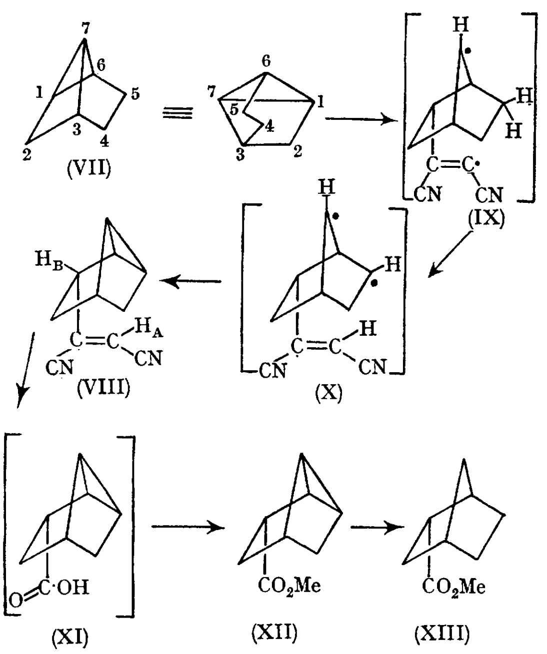
(IV)



(V) (VI)

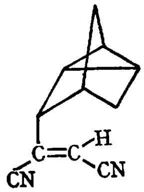
We report that, although steric hindrance does not stop the reaction, slight differences in steric environment can completely control which end of a strained carbon–carbon single bond is attacked.

When tricyclo[4,1,0,$0^{3,7}$]heptane[5] (VII) was treated with dicyanoacetylene in a 1 : 1 ratio at 70° for 14 hours a crystalline product (46% yield) was formed. This material was shown to consist of 96% of the 1 : 1 adduct† (VIII), m.p. 58—59°.

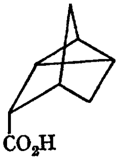


The 1 : 1 nature of the adduct was established by both chemical analysis and mass spectroscopy (*m/e* 170 for the parent ion). The ultraviolet spectrum of (VIII) had λ_{max} 22 mμ (ϵ 8250) suitable for a monosubstituted maleonitrile.[6] The near-infrared spectrum of (VIII) showed a maximum at 1·658 μ (ϵ 0·910) similar to absorptions previously noted for polycyclic molecules containing the cyclopropyl moiety.[4,7] The n.m.r. spectrum of (VIII) showed a single olefinic proton at τ 3·75 (doublet) which was coupled with the single allylic proton at τ 6·25 (J_{AB} 2·5 c./sec.). The remainder of the spectrum consisted of multiplets at τ 7·00 (1H), 7·40 (1H), and 8·00—8·60 (6H). The spectral data were consistent with either structure (VIII) or the nortricyclane derivative (XIV) (although the basic n.m.r. pattern for the nortricyclane skeleton differs somewhat from that observed).

In order to eliminate the possibility of (XIV) being our product, we degraded the 1 : 1 adduct *via* reaction with osmium tetroxide in pyridine–ether, work-up with hydrogen sulphide, and oxidation with basic hydrogen peroxide to yield a tricyclic acid‡ (XI) which was spectroscopically completely different from (XV),[8] thus eliminating (XIV) as the structure of the adduct. Esterification of (XI) with diazomethane gave (XII), which was spectroscopically different from the methyl ester of (XV).[8] The stereochemistry of the methoxycarbonyl group in (XII) was proved by the catalytic hydrogenation of (XII) over 5% Pd–C to yield only the known[9] *endo*-methoxycarbonylbicyclo[2,2,1]heptane (XIII), identical with an authentic sample.



(XIV)



(XV)

Since we have previously shown that electron-deficient carbon–carbon multiple bonds add to strained cyclopropanes *via* formation of diradical intermediates, we propose that (VIII) arises through the initial addition of dicyanoacetylene to the sterically less hindered C-1 position§ of (VII). Rear attack on the bent σ-bond would give the diradical (IX) which on hydrogen transfer would be converted into the new diradical (X). Closure of this diradical would give (VIII).¶

The formation of (VIII) in the addition of dicyanoacetylene firmly established that the "rear attack" of carbon–carbon multiple bonds on strained carbon–carbon single bonds is a general phenomenon. Furthermore, it conclusively demonstrated that, although steric hindrance

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† The low yield can be attributed to the product (VIII) being a derivative of (VII) and hence being able to react further with dicyanoacetylene.

‡ This acid was contaminated with small amounts (10—30% depending on reaction conditions) of an isomeric acid which probably results from base-catalyzed epimerization of (VIII) in the oxidation step.

§ Attack at the more hindered C-7 position would yield (XIV).

¶ An alternative mechanism which cannot be ruled out in the present case would involve a concerted 2 + 2 + 2 type of double "ene" reaction.

does not overcome this tendency for "rear attack," it does control which end of the strained σ-bond is attacked.

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