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DIELS-ALDER ADDITIONS OF DICYANOACETYLENE TO AROMATIC HYDROCARBONS

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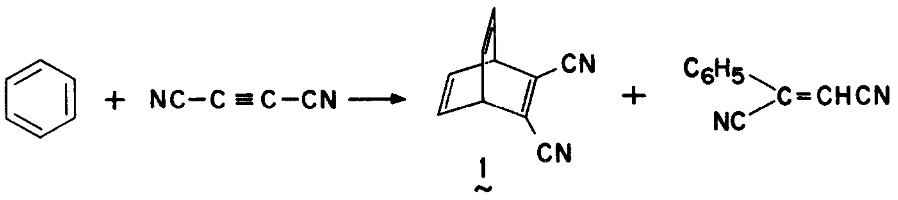
Only a few examples of Diels-Alder additions to monocyclic aromatic hydrocarbons are known so far. Benzyne (1) and hexafluoro-2-butyne (2) add to benzene, and the adducts of hexafluoro-2-butyne (2) and dicyanoacetylene (3) to durene have been prepared. We have found that 2,3-dicyanobicyclo[2.2.2]-octa-2,5,7-triene (**1**) is formed in 14% yield when a solution of dicyanoacetylene in benzene is heated to 180° for two days, and that the reaction is strongly accelerated by aluminum chloride. In the presence of this Lewis acid, the addition proceeded at room temperature to furnish compound **1** in 63% yield in addition to the Friedel-Crafts products phenylmaleonitrile (4%) and phenylfumaronitrile (11%). 2,3-Dicyanobicyclo[2.2.2]octa-2,5,7-triene (**1**), m.p. 132-133°, λ_{max}^{MeCN} 315 mμ (ε 830) and 232 mμ (ε 5700), was identified by its nmr spectrum (in $CDCl_3$), which showed multiplets at τ 3.1 (4H) and τ 4.9 (2H), and by catalytic hydrogenation to a tetrahydro derivative, 2,3-dicyanobicyclo-[2.2.2]oct-2-ene (**2**), which was identical with the hydrogenation product of the adduct **3** (3) of dicyanoacetylene and 1,3-cyclohexadiene.



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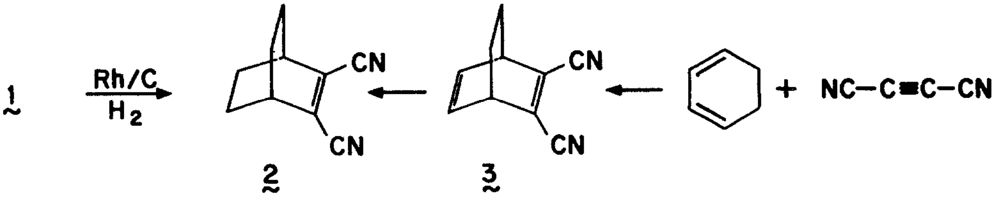
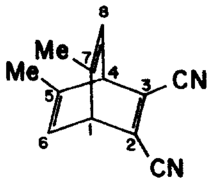


Thermal addition of dicyanoacetylene to p-xylene at 160° furnished a mixture of the two adducts **4** and **5** (ratio 70:30) in low yield. The nmr spectrum of 2,3-dicyano-5,7-dimethylbicyclo[2.2.2]octa-2,5,7-triene (**4**),



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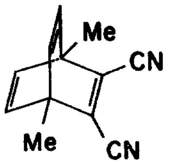

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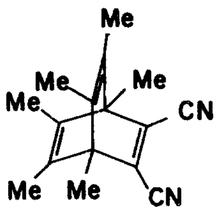

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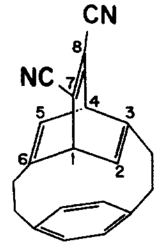
m.p. 97-98°, λ_{max}^{MeCN} 339 mμ (ε 450) and 237 mμ (ε 5500), showed the olefinic protons as a multiplet at τ 3.7 (2H), the bridgehead protons as a doublet ($J_{1,6}$ = 6 cps) split into doublets ($J_{1,8}$ = 2 cps) at τ 5.4 (2H) and the methyl groups as a doublet ($J_{6,Me}$ = 2 cps) at τ 8.0 (6H). Singlets at τ 3.5 (4H) and 8.1 (6H) were the only signals in the nmr spectrum of 2,3-dicyano-1,4-dimethylbicyclo[2.2.2]octa-2,5,7-triene (**5**), m.p. 118-120°, λ_{max}^{MeCN} 318 mμ (ε 810) and 234 mμ (ε 5300). In the presence of aluminum chloride and aluminum bromide, addition again occurred at room temperature and the adducts **4** and **5** were formed in ratios of 20:80 and 50:50, respectively. The yields were lower than in the case of benzene since the Friedel-Crafts reaction became more prominent.

The catalytic action of the aluminum halides was suppressed in nitromethane or just by addition of an equimolar amount (relative to the catalyst) of ether to the reaction mixture. Aluminum chloride was not effective in catalyzing the addition of dicyanoacetylene to chlorobenzene and anisole, nor in promoting the addition of cyanoacetylene, dimethyl acetylenedicarboxylate, and hexafluoro-2-butyne to benzene.

Lewis-acid catalysis of the Diels-Alder reaction has been known for sometime (4), although no such effect in additions to benzene or its derivatives appears to have been reported so far. The reaction is believed to proceed *via* a complex of the dienophile or diene with the Lewis acid; evidence for such complexes has been obtained by infrared spectroscopy (5). In the case of dicyanoacetylene and aluminum bromide, an insoluble 1:1 complex could be obtained by combining cyclohexane solutions of the two components. The complex reacted with benzene and *p*-xylene to produce **1**, and **4** and **5**, respectively, and is thus most likely an intermediate in the above described reactions. Competition experiments showed that reaction of the dicyanoacetylene-aluminum bromide complex with *p*-xylene at 25° is faster by a factor of 400 than the corresponding addition to benzene. In the thermal (160°) uncatalyzed reaction, this factor was found to be 16. The difference in relative rates does not appear large enough to postulate different mechanisms for the catalyzed and thermal additions of dicyanoacetylene to aromatic hydrocarbons.

The fact that methyl substituents facilitate Diels-Alder additions to aromatic hydrocarbons is further illustrated by isolation of adduct **6** in 83% yield from the uncatalyzed addition of dicyanoacetylene to hexamethylbenzene in benzene at 130°. That strain in the aromatic hydrocarbon also lowers the activation barrier for such additions is borne out by the formation of 1:1 and 2:1 adducts of dicyanoacetylene and [2.2]paracyclophane at relatively low temperatures. At 120°, the two compounds combine to give a mixture of the 1:1 adduct 7 and the 2:1 adduct **8** in 32 and 39% yield, respectively. At 170°, only **8** is formed (72% yield). The nmr spectrum of adduct **7**, m.p. 221-222°, λ_{max}^{MeCN} 357 mμ (ε 600), 292 mμ (ε 900), 284 mμ (ε 1100) 278 mμ (ε 1100) and 233 mμ (ε 11,600), showed the aromatic protons as a singlet at τ 3.03, the olefinic protons as a doublet ($J_{1,2}$ = 5.8 cps; split again extensively) at τ 4.3, the bridgehead protons as a doublet ($J_{1,2}$ = 5.8 cps), split into doublets ($J_{1,5}$ = 1.8 cps), at τ 5.80 and the methylene protons as a multiplet at τ 6.8-7.9. The 2:1 adduct **8** could be sublimed without change at 210°



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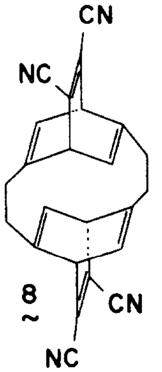

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(0.01μ); it turned dark at 280° and melted with decomposition at 295°. Its ultraviolet spectrum showed maxima at 350 mμ (ε 620) and 239 mμ (ε 9000). Its nmr spectrum was determined in hexafluoroacetone deuterate since no other suitable solvent could be found; it displayed the four olefinic protons as a poorly resolved doublet at τ 3.7 and the eight methylene protons as a broad band at τ 7.0-7.7. The bridgehead protons occurred at τ 5.3, under a band due to small amounts of water present in the solvent. The fact that this signal corresponded to four protons was ascertained by integration of a blank sample of the solvent. The 2:1 adduct 8 can exist in two stereoisomeric forms, depending on how the two bicyclooctatriene molecules are connected. In one isomer, the two dicyanoethylene bridges are approximately parallel to each other, in the other they form an angle of *ca.* 60-90°, depending on the conformation of the ethano bridges. It is not known whether the product isolated is a single isomer or a mixture of the two. To our knowledge, compounds 7 and 8 are the first Diels-Alder adducts of [2.2]paracyclophane to be isolated (6).

The chemistry and photochemistry of the dicyanobicyclo[2.2.2]-octatrienes reported in this Communication will be the subject of later publications.

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