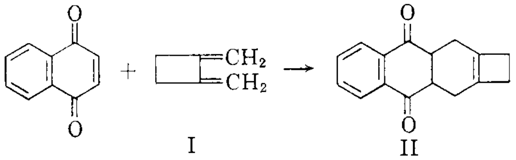
Anomalous Diels-Alder Reaction of 2,3-Dicyano-*p*-benzoquinone with 1,2-Dimethylenecyclobutane

H. D. Hartzler and R. E. Benson

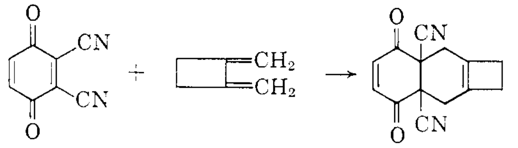
Received April 6, 1961

Diels-Alder additions to substituted *p*-benzoquinones normally occur at the least hindered double bond and at very slow rates if angular substituents are thereby formed.[1] A recent communication[2] reported preferential attack at the more hindered side when the benzoquinone bore strong electron-withdrawing substituents. We have obtained similar results in the reaction of 2,3-dicyano-*p*-benzoquinone with 1,2-dimethylenecyclobutane (I).

Reactions of I with quinones have been studied,[3] and a typical reaction is that with 1,4-naphthoquinone to give II. With 2,3-dicyano-*p*-benzoquinone, however, the reaction occurs predominantly at the more hindered double bond to give III.



I II



III

Moreover, in spite of the unfavorable geometry, the reaction is very rapid, being complete within five minutes at 80° as judged by the disappearance of the red color of the charge-transfer complex. The great reactivity of the dicyanoquinone may undoubtedly be attributed to the low electron density of the double bond to which are attached four electron-withdrawing groups.[4]

The structure of III was confirmed by its infrared and NMR spectra. The latter showed unsaturated CH and two types of saturated CH roughly in the ratio of 1:2:2. The infrared spectrum showed absorption due to nonconjugated C≡N at 4.43 μ, conjugated C═C at 6.2 μ, C═O at 5.8 μ, and both saturated and unsaturated CH. The position of the carbonyl stretching frequency as if it were nonconjugated may be rationalized with the assumption that the inductive effect of the cyano group counterbalances the resonance interaction of the carbonyl with the ethylenic double bond.

EXPERIMENTAL

1,2,3,3a,4,7,7a,8-Octahydro-4,7-dioxocyclobuta[b]naphthalene 3a,7a-dicarbonitrile (III). 2,3-Dicyano-*p*-benzoquinone[5] (2.37 g., 15 mmoles) and allene dimer[6] (1.50 g. of a mixture containing 85% 1,2-dimethylenecyclobutane) were heated under nitrogen at reflux in 100 ml. of benzene containing a trace amount of *p*-*t*-butylcatechol. An initial red color changed to pale yellow within 5 min. Evaporation of the solvent left an oil which was crystallized by the addition of 10 ml. of pentane. Filtration gave 3.64 g. of the crude adduct, m.p. 63–90°. Three crystallizations from cyclohexane gave III as a white crystalline solid, m.p. 104.5–105.6°. The yield of purified material was 2.07 g., 58%.

Anal. Calcd. for $C_{14}H_{10}N_2O_2$: C, 70.6; H, 4.24; N, 11.8. Found: C, 70.3; H, 4.35; N, 12.1.

The NMR spectrum of III in deuterochloroform solution using tetramethylsilane as an internal standard showed peaks at τ^7 = 3.03, 7.22, and 7.42 corresponding to the vinyl protons and the two types of methylene protons respectively.

Central Research Department
Experimental Station
E. I. du Pont de Nemours and Co., Inc.
Wilmington, Del.

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(1) J. A. Norton, *Chem. Rev.*, **31**, 319 (1942).

(2) M. F. Ansell, G. C. Culling, B. W. Nash, and D. A. Wilson, *Proc. Chem. Soc.*, 405 (1960).

(3) H. N. Cripps, U. S. Patent **2,934,544** (1960).

(4) The outstanding case in point is the extraordinary reactivity of tetracyanoethylene in Diels-Alder reactions; *cf.*, W. J. Middleton, R. E. Heckert, E. L. Little, and C. G. Krespan, *J. Am. Chem. Soc.*, **80**, 2783 (1958).

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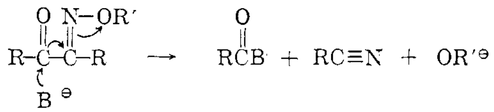
The Effect of Steric Hindrance on the Second-Order Beckmann Rearrangement[1]

Jeremiah P. Freeman

Received February 9, 1961

Two mechanisms have been proposed for the "second-order" Beckmann rearrangement of benzil monoxime esters. One involves attack of a base on the carbonyl group with concerted fragmentation of the rest of the molecule.[2] The second suggests



$$\underset{\underset{B^{\ominus}}{\uparrow}}{R-\overset{O}{\overset{\|}{C}}}-\overset{N-OR'}{\overset{\|}{C}}-R \longrightarrow R\overset{O}{\overset{\|}{C}}B + RC\equiv N + OR'^{\ominus}$$

that fragmentation occurs first to produce an incipient acyl carbonium ion which reacts with solvent or any available base.[3]

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(1) This research was carried out under U. S. Army Ordnance Contract DA-01-021-ORD-11878.

(2) A. G. Green and B. Saville, *J. Chem. Soc.*, 3887 (1956).

(3) A. F. Ferris, G. E. Johnson, and F. E. Gould, *J. Org. Chem.*, **25**, 1813 (1960) and preceding articles.