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

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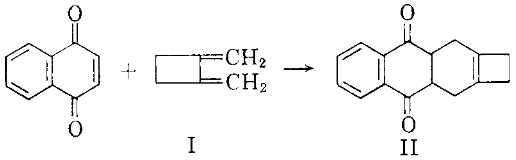
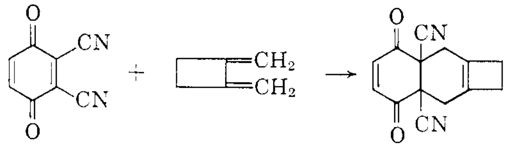
Diels-Alder additions to substituted *p*-benzoquinones normally occur at the least hindered double bond and at very slow rates if angular substituents are thereby formed.[1] A recent communication[2] reported preferential attack at the more hindered side when the benzoquinone bore strong electron-withdrawing 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.

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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).

[5] J. Thiele and F. Günther, *Ann.*, 349, 45 (1906).

[6] J. K. Williams and W. H. Sharkey, *J. Am. Chem. Soc.*, 81, 4269 (1959).

[7] G. V. D. Tiers, *J. Phys. Chem.*, 62, 1151 (1958).

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

Jeremiah P. Freeman

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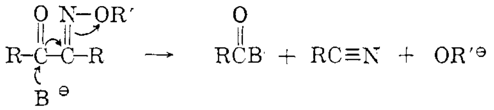
Two mechanisms have been proposed for the "second-order" Beckmann rearrangement of benzil monoxime esters. One involves attack of a base on the carbonyl group with concerted fragmentation of the rest of the molecule.[2] The second suggests



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

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

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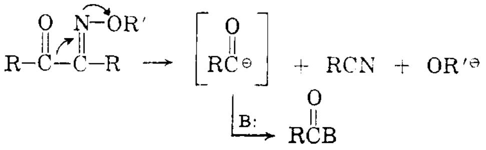
[1] This research was carried out under U. S. Army Ordnance Contract DA-01-021-ORD-11878.

[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.

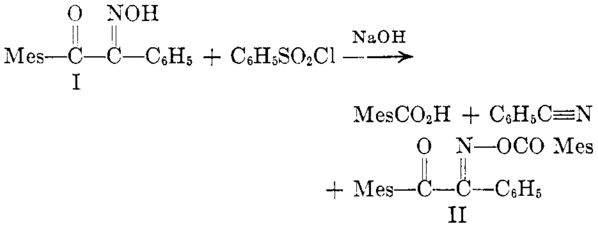


$$\mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{N-OR'}{\|}}{C}{-}R} \longrightarrow \left[\mathrm{R\overset{\overset{O}{\|}}{C}{}^{\ominus}}\right] + \mathrm{RCN} + \mathrm{OR'^{\ominus}}$$

$$\xrightarrow{\mathrm{B:}} \mathrm{R\overset{\overset{O}{\|}}{C}B}$$

The first mechanism seemed preferable to us because it better explained the role of the base necessary for the reaction. It appeared that by using a benzil monoxime which was sterically hindered about the carbonyl group a choice could be made between the two mechanisms. Mesitoyl phenyl ketoxime[4] (I) was chosen, as this ketone is unreactive toward nucleophilic attack.[5] Also, whereas benzil monoxime was degraded in the second-order Beckmann fashion when treated with perchloryl fluoride, the ketoxime I was merely converted to the corresponding benzil with no cleavage.[6]

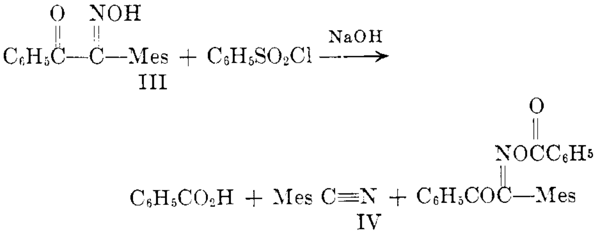
However, when ketoxime I was treated in sodium hydroxide solution with benzenesulfonyl chloride, conditions identical to those used by Ferris,[3] the second-order Beckmann cleavage occurred readily. Mesitoic acid and benzonitrile were obtained as the major products, but a trace of mesitoyl phenyl ketoxime mesitoate (II) was also produced. Oxime esters are often obtained from these reactions.[3,6]



$$\underset{\mathrm{I}}{\mathrm{Mes{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{NOH}{\|}}{C}{-}C_6H_5}} + \mathrm{C_6H_5SO_2Cl} \xrightarrow{\mathrm{NaOH}} \mathrm{MesCO_2H} + \mathrm{C_6H_5C{\equiv}N} + \underset{\mathrm{II}}{\mathrm{Mes{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{N-OCO\,Mes}{\|}}{C}{-}C_6H_5}}$$

Mes = 2,4,6-$(CH_3)_3C_6H_2$—

The isomeric oxime, benzoyl mesityl ketoxime (III) was prepared by the nitrosation of α-mesitylacetophenone; this reaction is an interesting example of the ineffectiveness of steric hindrance. Under the second-order Beckmann conditions, this ketoxime produced mesitonitrile and benzoyl mesityl ketoxime benzoate (IV). Benzoic acid was present also but in lesser amount.



$$\underset{\mathrm{III}}{\mathrm{C_6H_5\overset{\overset{O}{\|}}{C}{-}\overset{\overset{NOH}{\|}}{C}{-}Mes}} + \mathrm{C_6H_5SO_2Cl} \xrightarrow{\mathrm{NaOH}} \mathrm{C_6H_5CO_2H} + \mathrm{Mes\,C{\equiv}N} + \underset{\mathrm{IV}}{\mathrm{C_6H_5CO\overset{\overset{NO\overset{O}{\overset{\|}{C}}C_6H_5}{\|}}{C}{-}Mes}}$$

These experiments do not unequivocally settle the question of mechanism although they add to the evidence submitted by Ferris.[3] The reactivity of the benzenesulfonate of ketoxime I toward nucleophilic reagents parallels that of mesitoyl chloride which is known to react by an ionization mechanism.[7,8] The aqueous medium employed for these reactions is an ideal one for promoting ionization. It is probable that the conditions employed by Ferris[9] in attempting to use amines in inert solvents for this reaction were unsuitable for promoting ionization as were those in the experiments with ketoxime I and perchloryl fluoride (dry tetrahydrofuran).[6] The fact that more oxime ester was obtained from the less hindered carbonyl compound III may indicate that both mechanisms for the cleavage are operative; in the presence of a good nucleophile and no hindrance, the concerted mechanism is followed; when this path cannot be followed because of steric hindrance, the fragmentation process may occur.

EXPERIMENTAL

Reaction of mesitoylphenyl ketoxime with benzenesulfonyl chloride and base. To a solution of 2.0 g. (0.05 mole) of sodium hydroxide in 50 ml. of water was added 2.7 g. (0.1 mole) of mesitoyl phenyl ketoxime.[4] After solution was complete, 2.2 g. (0.012 mole) of benzenesulfonyl chloride was added with stirring; the temperature was not allowed to exceed 40°. The mixture was stirred at room temperature overnight, then extracted with ether, and acidified. The solid that precipitated was identified as mesitoic acid, m.p. 152–154°, mixed melting point with authentic sample, 152–154°; yield 1.3 g. (80%).

The ether extracts, after being dried and concentrated, yielded a yellow oil, which was chromatographed on silica. Pentane–methylene chloride (3:1) eluted benzonitrile identified by its infrared spectrum; yield 0.5 g. (56%). Methylene chloride eluted a viscous liquid which crystallized from hexane, m.p. 122–123°; yield 0.05 g.

Anal. Calcd. for $C_{27}H_{27}NO_3$: C, 78.38; H, 6.58; N, 3.38. Found: C, 78.35, 78.41, 78.29; H, 6.75, 6.41, 6.50; N, 3.40.

Its infrared spectrum showed two carbonyl groups, one at 1690 cm.$^{-1}$ attributable to a hindered ketone and the other at 1768 cm.$^{-1}$ attributable to a hindered oxime ester. Finally, an authentic specimen of the material, *mesitoyl phenyl ketoxime mesitoate* (II), was prepared from mesitoylphenyl ketoxime and mesitoyl chloride by the method described for oxime benzoates.[10]

α-Mesitylacetophenone. To 7.92 g. (0.06 mole) of aluminum chloride suspended in 50 ml. of dry benzene was added a solution of 10.0 g. (0.05 mole) of mesitylacetyl chloride, prepared from mesitylacetic acid and thionyl chloride, in 50 ml. of dry benzene slowly at 0–10°. The mixture was allowed to warm to room temperature and was stirred there for 3 hr. It was worked up in the usual manner to yield 6.9 g. (58%) of α-mesitylacetophenone, m.p. 147–148° (from ethanol).

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[4] A. Weissberger and D. B. Glass, *J. Am. Chem. Soc.*, **64**, 1724 (1942).

[5] H. H. Weinstock and R. C. Fuson, *J. Am. Chem. Soc.*, **58**, 1233 (1936).

[6] J. P. Freeman, *J. Am. Chem. Soc.*, **82**, 3869 (1960).

[7] D. A. Brown and R. F. Hudson, *J. Chem. Soc.*, 3352 (1953). For further discussion of this point, see M. S. Newman, *Steric Effects in Organic Chemistry*, John Wiley and Sons, Inc., New York, 1956, p. 225.

[8] For a discussion of fragmentation reactions of this type, see C. A. Grob, *Kekule Symposium on Theoretical Organic Chemistry*, Butterworths, London, England, 1959, p. 114.

[9] A. F. Ferris, G. E. Johnson, and F. E. Gould, *J. Org. Chem.*, **25**, 496 (1960).

[10] C. R. Hauser and G. Vermillion, *J. Am. Chem. Soc.*, **63**, 1224 (1941).

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.67; H, 7.62. Found: C, 85.62; H, 7.46.

Benzoyl mesityl ketoxime. The nitrosation method of Weissberger and Glass[4] was followed using 4.75 g. (0.02 mole) of α-mesitylacetophenone and 1.5 g. (0.035 mole) of butyl nitrite. Benzoyl mesityl ketoxime was obtained as a white solid, m.p. 158–159° (from ethanol); yield 2.0 g. (37%).

Anal. Calcd. for $C_{17}H_{17}NO_2$: C 76.38; H 6.41; N, 5.24. Found: C, 76.92, 76.59; H, 6.45, 6.21; N, 5.32.

Reaction of benzoyl mesityl ketoxime with benzenesulfonyl chloride and base. The reaction was run in the manner described above using 0.9 g. (0.0033 mole) of benzoyl mesityl ketoxime, 0.73 g. (0.004 mole) of benzenesulfonyl chloride, and 0.66 g. (0.016 mole) of sodium hydroxide in 25 ml. of water. The ether extracts of the alkaline solution yielded a yellow oil which was chromatographed as before to yield 0.15 g. (31%) of mesitonitrile (identified by its infrared spectrum) and 0.4 g. (67%) of a solid, m.p. 127–129°, believed to be *benzoyl mesityl ketoxime benzoate.* Infrared bands: $\gamma_{C=O}$ 1650 cm.$^{-1}$,$\gamma_{C=O}$ 1745 cm.$^{-1}$ Recrystallization was effected from ethanol.

Anal. Calcd. for $C_{24}H_{21}NO_3$: C, 77.61; H, 5.70; N, 3.77; Found: C, 77.23, 77.65; H, 6.23, 6.18; N, 3.52.

Acidification of the alkaline solution yielded 0.05 g. (12%) of benzoic acid.

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The *ortho*-Claisen Rearrangement. VII. The Rearrangement of Allyl *p*-Tolyl-2,6-d_2 Ether[1]

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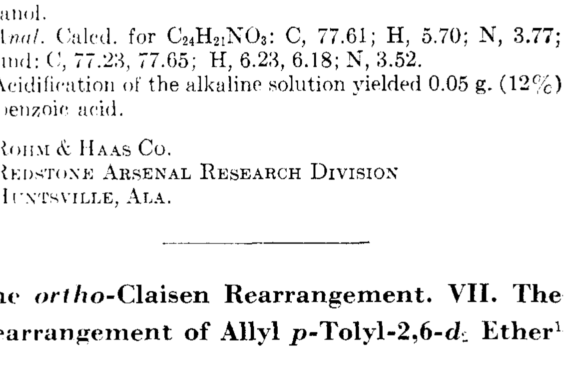
The sequence of reaction steps comprising the *ortho*-Claisen rearrangement is usually written as:



It has been suggested[4] that neither step 1 nor step 2 is reversible and that step 1 is slow and rate-determining. This appears to be an eminently reasonable assumption since enolization (step 2) is ordinarily a very facile reaction whereas the breaking and forming of carbon-oxygen and carbon-carbon bonds (step 1) does not occur so easily.[5] Indeed this has usually been tacitly assumed in the interpretation of kinetic studies of this reaction.[6,7] However, it was desirable to demonstrate that the above kinetic scheme is a true representation of the facts.

This demonstration could be accomplished by determining whether there was a kinetic isotope effect in the rearrangement of allyl *p*-tolyl-2,6-d_2 ether or whether isotope fractionation occurred in the rearrangement of a mixture of allyl *p*-tolyl-2,6-d_2 ether and ordinary allyl *p*-tolyl ether. A kinetic isotope effect would indicate that the step involving carbon-hydrogen bond breaking must determine, at least in part, the over-all rate of reaction. Isotope fractionation would occur if step 1 was reversible and step 2 was rate-controlling.

RESULTS AND DISCUSSION

Allyl *p*-tolyl-2,6-d_2 ether was prepared by a sequence of reactions starting with *p*-toluidine. A sample of *p*-toluidine was heated at 120° for ten hours with deuterium chloride in deuterium oxide. This treatment was repeated with a fresh portion of deuterium oxide four times. The deuterated toluidine was diazotized and the diazonium solution decomposed to yield *p*-cresol-2,6-d_2. The cresol was converted to allyl *p*-tolyl-2,6-d_2 ether by treatment with allyl bromide in the presence of potassium carbonate.

Combustion of the 3,5-dinitrobenzoate of the *p*-cresol-2,6-d_2 to water followed by reduction of the water to hydrogen and mass spectrometric analysis of the latter showed that the cresol contained 1.51 atoms of deuterium per molecule. A sample of the *p*-cresol-2,6-d_2 was brominated to 2,6-dibromo-*p*-cresol. A similar analysis of the 3,5-dinitrobenzoate of this substance revealed 0.003 atom of deuterium per molecule of 2,6-dibromo-*p*-cresol. This indicates that almost all of the deuterium was incorporated into the 2- and 6- positions of *p*-cresol.

The kinetics of rearrangement of allyl *p*-tolyl-2,6-d_2 ether and allyl *p*-tolyl ether were determined spectrophotometrically in carbitol as solvent. The specific rate constants for the rearrangement of these ethers at three temperatures are listed in Table I. The reactions were followed to 72–75% completion in each case, with seven points being determined in each run. The activation parameters were calculated by standard methods[8] and are also listed in Table I. Using the deviation listed for the individual rate constants, the mean statistical error

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(1) This investigation was supported in part by research grant NSF-G 7345 from the National Science Foundation.

(2) General Electric Foundation Fellow, 1960–61.

(3) From the thesis submitted by Eugene F. Wolfarth in partial fulfillment of the requirements for the Degree of Doctor of Philosophy at The Ohio State University.

(4) H. Schmid, *Helv. Chim. Acta*, **20**, 13 (1957).

(5) However, it has been shown that 6-allyl-2,6-dimethyl-2,4-cyclohexadienone rearranges with incredible ease to allyl 2,6-dimethylphenyl ether (the reverse of step 1) and 4-allyl-2,6-dimethylphenol [D. Y. Curtin and R. J. Crawford, *J. Am. Chem. Soc.*, **79**, 3156 (1957)].

(6) W. N. White, D. Gwynn, R. Schlitt, C. Girard, and W. Fife, *J. Am. Chem. Soc.*, **80**, 3271 (1958).

(7) W. N. White and B. E. Norcross, *J. Am. Chem. Soc.*, **83**, 1968 (1961) and W. N. White and W. K. Fife, *J. Am. Chem. Soc.*, in press.

(8) A. A. Frost and R. G. Pearson, *Kinetics and Mechanisms*, John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 95–97.