Stereochemistry of the Bis(1,3-cyclohexadiene)-*p*-Benzoquinone Adduct. A ^{13}C and X-ray Study

Richard K. Hill,* M. Gary Newton, Nantelle S. Pantaleo, and Kim M. Collins

Department of Chemistry, University of Georgia, Athens, Georgia 30602

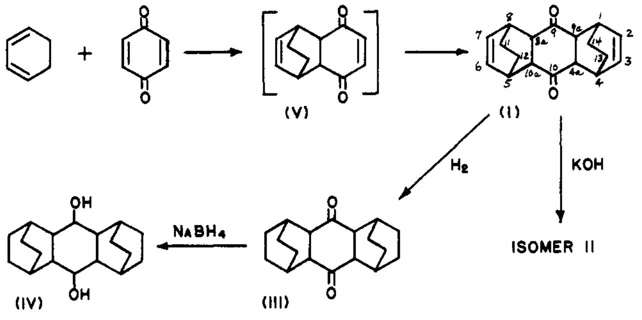
Received August 7, 1979

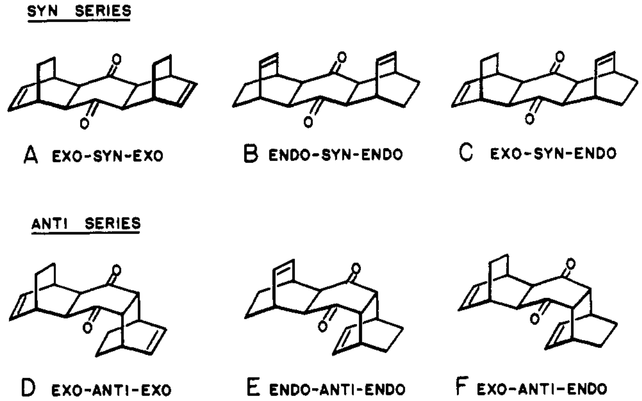
The Diels-Alder adduct formed from *p*-benzoquinone and 2 mol of 1,3-cyclohexadiene has been shown by ^{13}C NMR spectra of the adduct and its derivatives and by direct single-crystal X-ray crystallographic analysis to have the endo-anti-endo configuration E. Heating with alkali isomerizes the adduct to the exo-syn-endo isomer C.

The adducts of 1,3-dienes with *p*-benzoquinone occupy a special place in the history of the Diels-Alder reaction, as it was during the reinvestigation of an earlier incorrect structure proposal[1] for the cyclopentadiene-benzoquinone adduct that Diels and Alder realized the true nature of the reaction and first demonstrated its versatility.[2] The stereospecificity, which has proven to be such a valuable characteristic of the reaction, is exemplified in the adduct (I) formed[3] from *p*-benzoquinone and 2 mol of 1,3-cyclohexadiene: even when the possibilities are restricted to those structures containing only cis ring junctions there are still six possible stereoisomers (A-F) of I; however, only a single isomer is formed in the Diels-Alder reaction. Alder and Stein[4] showed that a second isomer (II) is produced by base-catalyzed isomerization of the adduct.

Beyond showing that the ring junctions in several diene-quinone adducts were cis, Alder and Stein were unable to assign configurations from among this array of possibilities. They suggested, however, that the bis(butadiene), -(cyclopentadiene), and -(1,3-cyclohexadiene) adducts belonged to the syn series and that the latter two were isomerized by base to the anti series. These early conjectures were later shown to be incorrect. The bis(butadiene) adduct was shown both in our laboratory[5] and by Crossley and Henbest[6] to be the cis-anti-cis isomer, while three different groups have demonstrated that the bis(cyclopentadiene) adduct is endo-anti-endo (corresponding to E): Winstein and co-workers[7] deduced the configuration by resolution of derivatives, Cookson et al.[8] showed the endo orientation by photochemical ring closure to a caged derivative, and Mills and co-workers[9] proved the configuration conclusively by single-crystal X-ray analysis. The configuration of the bis(diene) adducts is governed by three stereochemical considerations:[10] cis addition, endo orientation, and anti relation of the two diene moieties.

In view of these precedents and predictive rules, it is to be expected that the bis(cyclohexadiene) adduct (I), whose configuration had not been determined, has the endo-anti-endo stereostructure E. We report in this paper confirmation of this expectation by two independent and unambiguous methods.





Results and Discussion

The difference in symmetry properties between the syn and anti series makes it possible to apply a simple but powerful technique not previously used in stereochemical investigations of quinone-diene adducts: ^{13}C NMR spectroscopy. The central ring in structures A-F can rapidly interchange between two boat conformations; if the time-averaged planar conformation is used in the analysis of ^{13}C spectra, it can be seen that the fundamental (saturated) syn skeleton has C_{2v} symmetry, while the anti skeleton belongs to point group C_{2h}.

(a) The first step in the ^{13}C analysis is to measure the number of signals in the spectrum of the adduct itself, since this answers the question of whether the two diene moieties have added symmetrically, i.e., both endo or both exo. In the syn series, both the exo-exo and endo-endo adducts A and B have C_{2v} symmetry and would show five signals in the ^{13}C spectrum, while the exo-endo isomer C has a single symmetry plane and would show nine signals. Similarly, in the anti series, the exo-exo and endo-endo adducts D and E possess C_{2h} symmetry and thus have five sets of equivalent carbons, while the exo-endo isomer F has a single symmetry plane and would give nine signals.

Experimentally, the ^{13}C spectrum shows five sharp signals in a rough intensity ratio of 2:2:2:2:1. This result demonstrates that the two diene units have added both exo or both endo and eliminates structures C and F from consideration.

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[1] W. Albrecht, *Justus Liebigs Ann. Chem.*, **348**, 31 (1906).

[2] O. Diels and K. Alder, *Justus Liebigs Ann. Chem.*, **460**, 111 (1928).

[3] K. Alder and G. Stein, *Ber. Dtsch. Chem. Ges.*, **62**, 2337 (1929).

[4] K. Alder and G. Stein, *Justus Liebigs Ann. Chem.*, **501**, 247 (1933).

[5] R. K. Hill and J. G. Martin, *Proc. Chem. Soc., London*, 390 (1959); R. K. Hill, J. G. Martin, and W. H. Stouch, *J. Am. Chem. Soc.*, **83**, 4006 (1961).

[6] N. S. Crossley and H. B. Henbest, *J. Chem. Soc.*, 4413 (1960).

[7] L. deVries, R. Heck, R. Piccolini, and S. Winstein, *Chem. Ind. (London)*, 1416 (1959).

[8] R. C. Cookson, R. R. Hill, and J. Hudec, *J. Chem. Soc.*, 3043 (1964).

[9] R. Brown, J. M. Bruce, D. W. Hudson, and O. S. Mills, *J. Chem. Soc., Perkin Trans. 2*, 132 (1974). For an earlier X-ray study of an unspecified tetrahydro derivative, see H. G. Norment, *Acta Crystallogr.*, **18**, 627 (1965).

[10] J. G. Martin and R. K. Hill, *Chem. Rev.*, **61**, 537 (1961).

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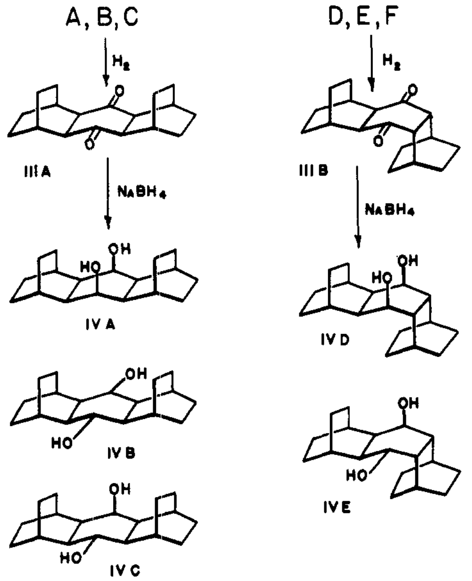
Scheme I



(b) The following symmetry arguments can be used to allow a choice between the syn and anti series. The adduct I was hydrogenated to the known tetrahydro derivative III; only two stereoisomers are possible, the syn (IIIa) and the anti (IIIb). Both of these possess symmetry elements which result in five sets of equivalent carbons. Reduction of III to diol IV does permit the syn vs. anti distinction to be made, however, as shown in Scheme I. The syn diketone can afford any of three diols IVa–c; because IVa and IVb still have C_{2v} symmetry, they will show only five ^{13}C signals, while IVc, with C_s symmetry, will show ten signals. The anti diketone IIIb, on the other hand, can yield only two diols, IVd,e. IVd has C_s symmetry and would show nine signals, while IVe has C_i symmetry (the time-averaged conformation has a center of symmetry) and would also show nine signals.

On the basis of these considerations, IIIa and IIIb can be distinguished simply by reduction to the diol mixture, isolation of a single stereoisomer, and measurement of its ^{13}C spectrum. In practice, III was reduced with $NaBH_4$ and a pure diol, mp 233–235 °C, was isolated by recrystallization from $CHCl_3$. The ^{13}C NMR spectrum showed nine signals, consistent only with IVd or IVe, proving that III and I belong to the anti series and ruling out A–C as possible structures for I. Confirmation that there was not a hidden tenth signal in the spectrum of IV was the appearance of the carbinol carbon signal as 65.5 ppm as a sharp *singlet*, consistent with the two equivalent carbinol carbons in IVd and IVe; isomer IVc, which would show ten signals, has *nonequivalent* carbinol carbons and would show two signals in this region.

(c) The results of the ^{13}C spectra of I and IV thus reduce the final choice of structure to D vs. E. Several experimental methods are conceivable to resolve this question, but it is sufficient to point out that Cookson et al. have proved[11] that the 1:1 adduct (V) of 1,3-cyclohexadiene and *p*-benzoquinone has the endo configuration; the proof involved irradiation to a saturated cage diketone, possible only for the endo isomer. Since the bis adduct I is formed via monoadduct V, I must have at least one endo fusion and must therefore be the endo–anti–endo isomer E.

It is also possible to deduce the structure of the isomer II formed by Alder and Stein by treatment of I with ethanolic KOH. If the reasonable assumptions are made (1) that this process involves only generation and subsequent protonation of carbanions next to the carbonyl groups rather than dissociation–recombination and (2) that under these equilibrating conditions II will not have any strained trans ring junctions, then only two structures can be formed by isomerizing the central ring junctions of E: the exo–anti–exo isomer D and the exo–syn–endo isomer C. These are easily distinguished by ^{13}C NMR, since C would show nine signals and D five. The spectrum of II shows nine sharp signals, proving it to be C. Since this isomerization occurs both with the adduct and its tetrahydro derivative III, the syn skeleton must be intrinsically more stable than the anti.

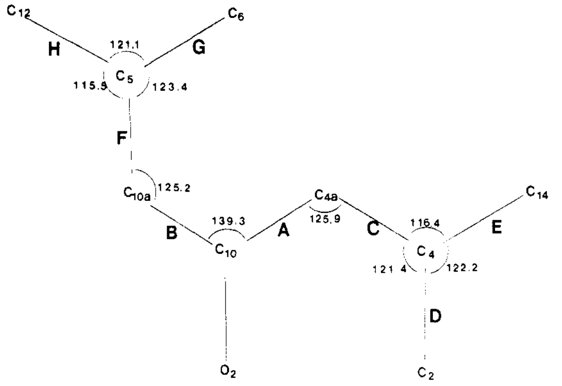


Figure 1. Idealized view of the bis-adduct structure perpendicular to the pseudo-mirror plane. The labels A–H refer to the best plane through the eight sets of atoms listed in Table III. The angles between these best planes are also shown.

Crystallographic Study. While these results serve as a striking example of the powerful ability of ^{13}C NMR to solve problems of distinguishing between isomers of different symmetry, it was desirable to have unambiguous confirmation by X-ray analysis. The crystallographic analysis confirms the endo–anti–endo configuration of the adduct deduced from the ^{13}C NMR data. Tables I and II list the bond lengths and angles calculated from the final position parameters. Bond lengths and angles correspond closely to those found by Brown et al.[9] and to commonly accepted values for C–C and C–O bonds. The bond elongation of C_{4a}–C_{9a} and C_{8a}–C_{10a} observed in the bis(cyclopentadiene)–quinone adduct (BCPQ) is not as pronounced in the current structure, but the bond lengths of C_1–C_{9a} (1.568 Å) and C_4–C_{4a} (1.576 Å) are 0.03 Å longer than normal C_{sp^3}–C_{sp^3} bonds. A similar effect is reported for BCPQ.

The dihedral angles given in Table III indicate that the structure is highly eclipsed conformationally and contains a pseudo-mirror plane of symmetry. Figure 1 presents an idealized view of the structure perpendicular to the pseudo-mirror plane. Best planes were calculated for each of the eight sets of atoms in Table III and are labeled A–H in Figure 1; angles between these best planes are also shown. As can be seen, the C_6–C_7 double bond is folded over the cyclohexanedione ring, which occupies a boat conformation. Plane D, which contains the C_2–C_3 double bond, is nearly parallel to the plane containing O_1–C_9–C_{10}–O_2. Angles between corresponding planes of the two cyclohexene rings are quite similar and indicate that little distortion is caused by close intramolecular contacts between the two ends of the molecule. The closest contacts occur between H(C_{4a})–C_6 (2.636 Å) and H(C_{9a})–C_7 (2.705 Å).

As previously mentioned, the diketone ring occupies a boat conformation with C_9 and C_{10} lying 0.447 and 0.494

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[11] R. C. Cookson, E. Crundwell, R. R. Hill, and J. Hudec, *J. Chem. Soc.*, 3062 (1964).

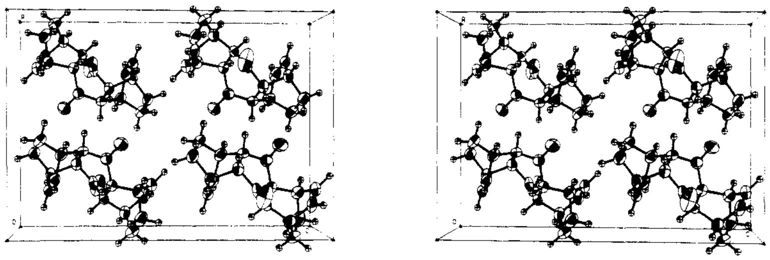

Figure 2. ORTEP stereodiagram of the molecular packing in the unit cell viewed down the *b* axis. The *c* axis is horizontal and the *a* axis is vertical.

Table I. Distances (Å) between Bonded Atoms[a]

C_1-C_2	1.498 (7)	C_{11}-C_{12}	1.538 (9)
C_1-C_{9a}	1.545 (6)	C_{13}-C_{14}	1.537 (9)
C_1-C_{14}	1.539 (8)	C_1-HC_1	1.01 (4)
C_2-C_3	1.318 (8)	C_2-HC_2	1.01 (4)
C_3-C_4	1.493 (7)	C_3-HC_3	1.01 (5)
C_4-C_{4a}	1.539 (6)	C_4-HC_4	0.99 (4)
C_4-C_{13}	1.546 (8)	C_{4a}-HC_{4a}	1.05 (3)
C_{4a}-C_{9a}	1.559 (6)	C_5-HC_5	1.05 (4)
C_{4a}-C_{10}	1.514 (6)	C_6-HC_6	0.97 (4)
C_5-C_6	1.502 (8)	C_7-HC_7	0.98 (4)
C_5-C_{10a}	1.571 (6)	C_8-HC_8	1.02 (4)
C_5-C_{12}	1.536 (7)	C_{8a}-HC_{8a}	1.01 (4)
C_6-C_7	1.313 (8)	C_{9a}-HC_{9a}	0.95 (4)
C_7-C_8	1.490 (7)	C_{10a}-HC_{10a}	0.96 (4)
C_8-C_{8a}	1.563 (7)	C_{11}-H_1C_{11}	0.99 (4)
C_8-C_{11}	1.553 (8)	C_{11}-H_2C_{11}	1.02 (4)
C_{8a}-C_9	1.503 (6)	C_{12}-H_1C_{12}	1.02 (4)
C_{8a}-C_{10a}	1.546 (7)	C_{12}-H_2C_1	1.00 (4)
C_9-C_{9a}	1.505 (6)	C_{13}-HC_{13}	1.01 (4)
C_9-O_1	1.209 (5)	C_{13}-H_2C_{13}	0.96 (4)
C_{10}-C_{10a}	1.502 (6)	C_{14}-H_1C_{14}	1.01 (4)
C_{10}-O_2	1.206 (6)	C_{14}-H_2C_{14}	1.01 (4)

[a] The estimated standard deviations given in parentheses do not contain cell constant errors, and bond lengths have not been corrected for thermal motion.

Å out of the C_{4a}–C_{9a}–C_{8a}–C_{10a} plane. In order to be consistent with the NMR results, the structure must be conformationally mobile in solution, rapidly interconverting between two alternate boat conformations. The average of these two conformations produces the equivalences observed in the NMR spectrum.

Figure 2 shows an ORTEP[12] stereodiagram of the molecular packing. The closest intermolecular contact is between $H(C_{9a})$–O_2 (2.430 Å) related by one unit cell translation along the *b* axis. There are six intermolecular contacts ≤2.6 Å.

In conclusion, both the ^{13}C NMR analysis and a definitive single-crystal structure prove the configuration of the bis(1,3-cyclohexadiene)-benzoquinone adduct to be endo-cis-anti-cis-endo. Like the other diene-quinone adducts, it is formed in a strikingly specific fashion by cis addition, endo orientation of diene and dienophile, and approach of the second diene from the more accessible face of the 1:1 adduct.

Experimental Section

The ^{13}C NMR spectra are proton decoupled.

Adduct I was prepared from 1,3-cyclohexadiene and resublimed *p*-benzoquinone as described by Alder and Stein.[4] Several recrystallizations from ethanol followed by recrystallization from ethyl acetate gave colorless needles: mp 196–198 °C (lit.[4] mp 196–197 °C); ^{13}C NMR ($CDCl_3$ with Me_4Si reference) 24.4, 32.4, 53.5, 133.6, 210.0 ppm.

Table II. Angles (deg) between Bonded Atoms

C_2-C_1-C_{9a}	108.2 (4)	C_3-C_4-HC_4	116 (2)
C_2-C_1-C_{14}	108.9 (4)	C_{4a}-C_4-HC_4	108 (2)
C_{9a}-C_1-C_{14}	107.0 (4)	C_{13}-C_4-HC_4	109 (2)
C_1-C_2-C_3	114.1 (4)	C_4-C_{4a}-HC_{4a}	109 (2)
C_2-C_3-C_4	114.8 (5)	C_{9a}-C_{4a}-HC_{4a}	108 (2)
C_3-C_4-C_{4a}	108.5 (4)	C_{10}-C_{4a}-HC_{4a}	106 (2)
C_3-C_4-C_{13}	108.6 (4)	C_6-C_5-HC_5	113 (2)
C_{4a}-C_4-C_{13}	106.8 (4)	C_{10a}-C_5-HC_5	108 (2)
C_4-C_{4a}-C_{9a}	108.7 (3)	C_{12}-C_5-HC_5	111 (2)
C_4-C_{4a}-C_{10}	112.6 (4)	C_5-C_6-HC_6	121 (2)
C_{9a}-C_{4a}-C_{10}	112.9 (4)	C_7-C_6-HC_6	125 (2)
C_6-C_5-C_{10a}	108.9 (4)	C_6-C_7-HC_7	122 (2)
C_6-C_5-C_{12}	108.1 (4)	C_8-C_7-HC_7	123 (2)
C_{10a}-C_5-C_{12}	106.5 (4)	C_7-C_8-HC_8	118 (2)
C_5-C_6-C_7	114.0 (5)	C_{8a}-C_8-HC_8	107 (2)
C_6-C_7-C_8	115.5 (5)	C_{11}-C_8-HC_8	108 (2)
C_7-C_8-C_{8a}	110.3 (4)	C_8-C_{8a}-HC_{8a}	106 (2)
C_7-C_8-C_{11}	107.1 (4)	C_9-C_{8a}-HC_{8a}	107 (2)
C_{8a}-C_8-C_{11}	105.7 (4)	C_{10a}-C_{8a}-HC_{8a}	109 (2)
C_8-C_{8a}-C_9	112.6 (4)	C_1-C_{9a}-HC_{9a}	109 (2)
C_8-C_{8a}-C_{10a}	108.9 (4)	C_{4a}-C_{9a}-HC_{9a}	107 (2)
C_9-C_{8a}-C_{10a}	113.2 (4)	C_9-C_{9a}-HC_{9a}	106 (2)
C_{8a}-C_9-C_{9a}	118.0 (4)	C_5-C_{10a}-HC_{10a}	107 (2)
C_{8a}-C_9-O_1	120.3 (4)	C_{8a}-C_{10a}-HC_{10a}	107 (2)
C_{9a}-C_9-O_1	121.7 (4)	C_{10}-C_{10a}-HC_{10a}	108 (2)
C_1-C_{9a}-C_{4a}	109.1 (4)	C_8-C_{11}-H_1C_{11}	107 (2)
C_1-C_{9a}-C_9	112.2 (4)	C_8-C_{11}-H_2C_{11}	112 (2)
C_{4a}-C_{9a}-C_9	113.7 (4)	C_{12}-C_{11}-H_1C_{11}	114 (3)
C_{4a}-C_{10}-C_{10a}	119.0 (4)	C_{12}-C_{11}-H_2C_{11}	110 (2)
C_{4a}-C_{10}-O_2	120.3 (4)	H_1C_{11}-C_{11}-H_2C_{11}	104 (3)
C_{10a}-C_{10}-O_2	120.7 (4)	C_5-C_{12}-H_1C_{12}	111 (2)
C_5-C_{10a}-C_{8a}	109 (4)	C_5-C_{12}-H_2C_{12}	109 (2)
C_5-C_{10a}-C_{10}	111.2 (4)	C_{11}-C_{12}-H_1C_{12}	106 (2)
C_{8a}-C_{10a}-C_{10}	114.1 (4)	C_{11}-C_{12}-H_2C_{12}	107 (2)
C_8-C_{11}-C_{12}	109.2 (5)	H_1C_{12}-C_{12}-H_2C_{12}	114 (3)
C_5-C_{12}-C_{11}	109.6 (4)	C_4-C_{13}-H_1C_{13}	110 (2)
C_4-C_{13}-C_{14}	109.5 (5)	C_4-C_{13}-H_2C_{13}	107 (3)
C_1-C_{14}-C_{13}	109.1 (5)	C_{14}-C_{13}-H_1C_{13}	111 (3)
C_2-C_1-HC_1	110 (2)	C_{14}-C_{13}-H_2C_{13}	111 (3)
C_9-C_1-HC_1	108 (2)	H_1C_{13}-C_{13}-H_2C_{13}	108 (4)
C_{14}-C_1-HC_1	115 (2)	C_1-C_{14}-H_1C_{14}	108 (3)
C_1-C_2-HC_2	121 (2)	C_1-C_{14}-H_2C_{14}	107 (2)
C_3-C_2-HC_2	124 (2)	C_{13}-C_{14}-H_1C_{14}	111 (3)
C_2-C_3-HC_3	125 (2)	C_{13}-C_{14}-H_2C_{14}	111 (2)
C_4-C_3-HC_3	120 (2)	H_1C_{14}-C_{14}-H_2C_{14}	111 (3)

Table III. Selected Dihedral Angles (deg)

atoms (I-J-K-L)[a]	angle (esd), deg	atoms (I-J-K-L)[a]	angle (esd), deg
C_1-C_2-C_3-C_4	0.5 (6)	C_9-C_{8a}-C_{10a}-C_{10}	4.5 (6)
C_1-C_{14}-C_{13}-C_4	0.7 (6)	C_8-C_{8a}-C_{10a}-C_5	3.4 (5)
C_1-C_{9a}-C_{4a}-C_4	−0.3 (5)	C_8-C_{11}-C_{12}-C_5	1.9 (6)
C_9-C_{9a}-C_{4a}-C_{10}	0.7 (5)	C_8-C_7-C_6-C_5	0.8 (6)

[a] The dihedral angle has a positive sign if the vector K–L is clockwise from vector J–I when viewed down vector J-K and a negative sign if counterclockwise.

Isomer II was prepared as described by Alder and Stein[4] by treatment of I with refluxing ethanolic KOH under nitrogen. Recrystallization from alcohol and then from ethyl acetate gave transparent hexagonal plates: mp 268–270 °C dec (lit.[4] mp 268

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[12] C. K. Johnson, "ORTEP: A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations", ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN, 1971.

Table IV. Summary of Crystallographic Data

molecular formula	$C_{18}H_{20}O_2$
mol wt	268.4
linear absorption coeff	0.88 cm^{-1} (Mo K$\bar{\alpha}$)
ρ(calcd)	1.274 g/cm^3
ρ(exptl)	1.273 g/cm^3
space group	$P2_1/c$
cell dimensions	a = 12.029 (5) Å
	b = 6.6447 (2) Å
	c = 17.49 (1) Å
	β = 90.23 (7)°
	Z = 4
	V = 1399 $Å^3$
no. of reflections measd	3500
no. of reflections obsd	759
final R	0.027
final R_w	0.023

dec); ^{13}C NMR ($CDCl_3$ with Me_4Si reference) 19.8, 23.8, 30.0, 30.1, 47.7, 54.3, 134.0, 134.4, 207.9 ppm.

The tetrahydro derivative III was prepared by hydrogenation in ethanol over 10% Pd/C, as described by Alder and Stein.[4] Recrystallization from ethyl acetate gave glistening flakes, mp 248–252 °C (lit.[4] mp 245 °C).

Diol IV. A suspension of 0.5 g of III in 25 mL of dry methanol was treated with 0.2 g of $NaBH_4$, refluxed 2 h, and stirred overnight at 25 °C. IR analysis showed that reduction was incomplete, so the product was heated at reflux with 0.3 g of $NaBH_4$ in 25 mL of methanol for 48 h. The cooled reaction mixture was diluted with water and extracted with ether (3 × 50 mL). The extracts were dried over $MgSO_4$ and concentrated, and the solid residue (still showing some carbonyl absorption in the IR spectrum) was recrystallized from $CHCl_3$. Colorless crystals (0.15 g, 30%) of a pure diol separated: mp 233–235 °C; IR (Nujol) 3250 (br, OH), no absorption between 1500 and 1800 cm^{-1}; ^{13}C NMR (Me_2SO-d_6 with Me_4Si reference) 19.8, 22.8, 22.9, 24.3, 26.6, 28.3, 40.7, 41.1, 65.5 ppm.

Crystal Structure Determination. The adduct was recrystallized from ethyl acetate and the sample used in the structure determination was cut from a longer needle crystal. All diffraction measurements were made on an Enraf-Nonius CAD-4 diffractometer using Mo K$\bar{\alpha}$ radiation and a graphite monochromator. The orientation matrix and cell dimensions were determined from 15 accurately centered reflections. Pertinent crystallographic information is summarized in Table IV.

Intensity data were corrected for Lorentz–polarization effects but not for absorption. In all, 759 unique nonzero reflections were used in the structural analysis. The structure was solved by the direct methods program MULTAN[13] (E's ≥ 1.4). The E map produced from phases with the highest ABSFOM value (3.38) revealed starting positions for the 20 nonhydrogen atoms. Refinement of these atomic positions and generation of a difference map gave starting positions for the 20 hydrogen atoms. Full-matrix least-squares refinement with anisotropic temperature factors for the carbon and oxygen atoms, isotropic temperature factors for hydrogen atoms, and weights of $1/\sigma_{F_o}$ gave a final R of 0.027 (R_w = 0.023).

Acknowledgment. We gratefully acknowledge the support of the National Science Foundation in the purchase of the JEOL PFT-100 NMR spectrometer on which the ^{13}C spectra were obtained.

Registry No. I, isomer E, 73035-87-7; II, isomer C, 73035-88-8; IIIB, 72952-87-5; IV, 72952-88-6; 1,3-cyclohexadiene, 592-57-4; *p*-benzoquinone, 106-51-4.

Supplementary Material Available: Table of positional coordinates and temperature factors (3 pages). Ordering information is given on any current masthead page.

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(13) Program MULTAN written by P. Main and M. U. Woolfson, University of York, York, England, and G. Germain, Universite de Louvain, Louvain, Belgium.

Quinone Dehydrogenation. Oxidation of Benzylic Alcohols with 2,3-Dichloro-5,6-dicyanobenzoquinone

Hans-Dieter Becker,* Anders Björk, and Erich Adler

Department of Organic Chemistry, Chalmers University of Technology and University of Gothenburg, S-412 96 Gothenburg, Sweden

Received November 23, 1979

2,3-Dichloro-5,6-dicyanobenzoquinone (DDQ) reacts with primary and secondary aryl-substituted alcohols under mild conditions in dioxane solution to give the corresponding carbonyl compounds in high yields. In contrast to other oxidants, DDQ can be applied advantageously for the oxidation of hydroxyaryl-substituted alcohols. A mechanism involving participation of the phenolic hydroxyl group in the dehydrogenation reaction is discussed. Oxidations of hydroxyaryl-substituted alcohols by DDQ in methanol solution resulting in the formation of benzoquinones by loss of the hydroxyalkyl side chain are interpreted in terms of phenol oxidation. An example of a pyridine-catalyzed Smiles rearrangement of an *o*-hydroxy-substituted diphenyl ether is reported.

High-potential quinones such as 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) or *o*-chloranil are well-established reagents for the conversion of allylic alcohols into the corresponding α,β-unsaturated carbonyl compounds.[1-4] By contrast, quinones have found only sporadic use, mainly in mechanistic studies, as oxidants for benzylic alcohols.[5,6] Long reaction times and low yields reported previously for the dehydrogenation of benzyl alcohol and diphenylcarbinol by *o*-chloranil may have discouraged preparative applications.[7]

In some analytical experiments, we had noted several years ago that DDQ smoothly oxidized, selectively, certain

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0022-3263/80/1945-1596$01.00/0 © 1980 American Chemical Society