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DIELS-ALDER ADDITION OF o-BENZOQUINONES TO CYCLOPENTADIENE

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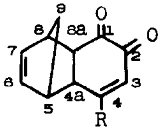
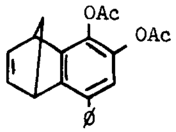
o-Benzoquinones can behave either as dienes or as dienophiles in Diels-Alder reactions. Usually, however, they react as dienes, particularly if they are substituted.(1) Recently we described(2) the isolation of Diels-Alder adducts from cyclopentadiene and three o-benzoquinones. In each case, the quinone functioned as the dienophile to give adducts 1, R=H, CH_3, or Ø.



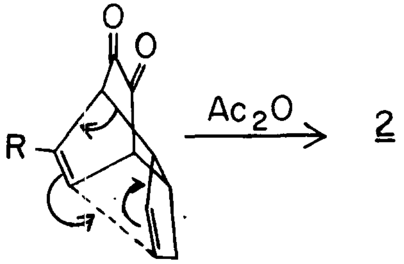
1



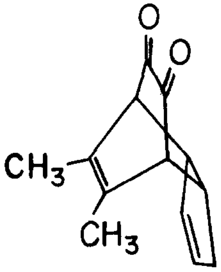
2

The phenylquinone adduct showed strong bands in its IR spectrum at 1720, 1660 and 1605 cm^{-1}, whereas the other two adducts absorbed at 1720, 1675 and 1635 cm^{-1}. These absorptions are consistent with the presence of conjugated and non-conjugated ketones. The NMR spectrum of the phenylquinone adduct was in accord with the proposed structure. Also the adduct was converted to the catechol diacetate 2 on treatment with acetic anhydride and pyridine.

Ansell and Gosden(3) suggested that the alternative structure 3, R=ϕ for the adduct could also account for the observed spectroscopic data. The isolation of 2 was



3



4

rationalized by the postulation that 3 rearranged to 1 during the reaction with acetic anhydride and pyridine.

In order to exclude this possibility, we examined our spectroscopic data again and compared them with those of the known 4,5-dimethyl-o-benzoquinone cyclopentadiene adduct(4) which has structure 4. The IR spectrum of 4 in both chloroform and KBr showed only one carbonyl band at 1725 cm^{-1} (cisoid α-diketones in 6-membered rings in bicyclic systems usually show two bands).* By analogy, compounds such as 3, R=H, CH_3, ϕ, would be expected to have only one band and certainly would not show a band in the 1660-1675 cm^{-1} region. The NMR spectrum of the dimethyl quinone adduct was in accord with structure 4. The methyl peaks at 8.15 and 8.25τ were quartets (J approximately 1 cps) due to homoallylic coupling. A broad series of peaks from 7.3 to 8.0τ of area two protons

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* Bicyclo[2.2.2]octane-2,3-dione(5) has bands at 1760 and 1731 cm^{-1}.

was assigned to the allylic methylene group and the vinyl protons were multiplets at 4.20 and 4.48τ.

The o-benzoquinone adduct had a spectrum readily interpretable in terms of structure 1, R=H but not in terms of structure 3, R=H. In particular, the vinyl region showed a two-proton multiplet at 3.92τ assigned to the 6,7-double bond and an AB part of an ABX system at 2.78 and 3.69τ with J_{AB}= 11 cps, J_{AX}= 4.5 cps and J_{BX}= 1.5 cps (by approximate first-order analysis). This is ascribed to coupling between the 3-,4- and 4a-protons of 1, R=H. No peaks were seen in the 7.3-8.0τ region but the methylene bridge protons were seen as a narrow multiplet at 8.38τ. The alternative structure 3, R=H would not have the ABX system and would show a spectrum in the high field region similar to that of 4.

The spectrum of the phenylquinone adduct already reported,(2) showed a singlet at 3.36τ which is not in agreement with structure 3, R=Ø as coupling between the vinyl proton and the adjacent bridgehead proton would be expected to be of the order of 5-6 cps.(6) The lack of allylic coupling between the 3- and 4a-protons compared with 1, R=H is probably due to a change in the geometry of the molecule.

The methylquinone adduct had a spectrum similar to that of 1, R=H. The vinyl region showed peaks at 3.91τ (m) assigned to the 6- and 7-protons and a broadened peak at 3.72τ due to the 3-proton. This broadening was caused by allylic coupling with the methyl group (which was a doublet at 7.88τ, J = 1 cps) and possibly by allylic coupling with the bridgehead proton. The bridge protons absorbed at 8.38τ.

The regions of the spectra containing the signals assigned to the cyclopentene ring were very similar in the spectra of 1, R=H and 1, R=CH_3 and were different from the corresponding regions in the spectrum of 4.

The ultraviolet spectra of three of the adducts were measured and the maxima are shown in the table.

TABLE

UV Spectra of o-Benzoquinonecyclopentadiene Adducts

Compound	mμ	ε
4	228 (sh) 302	1870 340
1 R=H	279	1700
1 R=CH_3	285	2250

The spectra of 1, R=H and 1, R=CH_3 were similar but were different from the spectrum of 4. This is indicative of the correctness of the structural assignments in these cases.

The spectral data presented in this paper demonstrate that the structures originally proposed for the adducts 1, R=H, CH_3 and ϕ are correct. By analogy with the corresponding p-benzoquinone cyclopentadiene adducts,(7) they probably have the cis-endo configuration.

As the yield(2) of purified adduct 1, R=CH_3 was less than 50%, the crude reaction product was examined by NMR spectroscopy to determine whether another isomer was present. The spectrum was essentially that of 1, R=CH_3, with an extra peak at 8.12τ. If this peak is assumed to be due to a methyl group, the crude product contained 85 ± 5% of 1, R=CH_3. The other material having the peak at 8.12τ was not identified. The spectrum of the crude 4,5-dimethyl-o-benzoquinone adduct 4 indicated that it was 80 ± 5% pure.

It is interesting to note that the introduction of another methyl group into 4-methyl-o-benzoquinone is sufficient to change the nature of the quinone from dienophile to diene.

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UV spectra were measured in methanol, NMR spectra in deuterochloroform, and the IR spectra in potassium bromide pellets or in chloroform.

REFERENCES

1. J. Sauer, Angew. Chem. Int. Ed., 5, 218 (1966).
2. F. J. Evans, H. S. Wilgus, III, and J. W. Gates, Jr., J. Org. Chem., 30, 1655 (1965).
3. M. F. Ansell and A. F. Gosden, Chem. Comm., 21, 520 (1965).
4. L. Horner and D. W. Baston, Chem. Ber., 98, 1252 (1965).
5. K. Alder, H. K. Schäfer, H. Esser, H. Krieger, and R. Ruebke, Ann., 593, 23 (1955).
6. Kazuo Tori, Yoshihiro Takano, and Keizo Kitahonoki, Chem. Ber., 97, 2798 (1964).
7. D. F. O'Brien and J. W. Gates, Jr., J. Org. Chem., 30, 2593 (1965).