Registry No. 1, 33948-32-2; 2, 38431-97-9; 3, 38432-00-7; 4, 71988-25-5; 4 methyl ester, 71988-26-6; 4 methyl ester, thio ketal, 71988-27-7; **5**, 71988-28-8; **6**, 71988-29-9; **7**, 71988-30-2; **7** dinitrophenylhydrazone, 71988-31-3; **8**, 38431-96-8; **9**, 38431-99-1; **10**, 71988-32-4; 11, 38431-98-0; **12**, 38432-01-8; **13**, 7499-70-9; **13** methyl ester, 57234-61-4; **13** methyl ester, thio ketal, 71988-33-5; **14**, 57234-59-0; **15**, 57234-63-6; **26**, 4594-78-9; **27**, 71988-34-6; **28**, 71988-35-7; **29**, 71988-36-8; **30a**, 71988-37-9; **30b**, 71988-38-0; **31**, 71988-39-1; **32**, 71988-40-4; **33**, 71988-41-5; **35**, 13672-62-3; **36**, 71988-42-6; **37a**, 54996-34-8; **37b**, 57155-71-2; **39**, 71988-43-7; **39** methyl ester, 71988-44-8; **40**, 71988-45-9; **41**, 71988-46-0; **42**, 71988-47-1; **43**, 71988-48-2; **44**, 71988-49-3; **46b**, 71988-50-6; **48b**, 71988-51-7; **51**, 71988-52-8; **52**, 71988-53-9; **53**, 15070-50-5; **54**, 71988-54-0; **54** acid, 71988-55-1; **55**, 71988-56-2; **56**, 71988-57-3; **57**, 71988-58-4; **58**, 71988-59-5; **59**, 71988-60-8; **60a**, 19214-14-3; **60b**, 71988-61-9; **60c**, 71988-62-0; **61**, 71988-63-1; **62a**, 71988-64-2; **62b**, 71988-65-3; **62b** dinitrophenylhydrazone, 71988-66-4; **63**, 71988-67-5; **64**, 71988-68-6; **65**, 71988-69-7; 2-oxocyclopenta-β-propionitrile, 4594-77-8; methyl vinyl ketone, 78-94-4; butylmercaptan, 109-79-5; methallyl chloride, 563-47-3; ethyl vinyl ketone, 1629-58-9; 1,2-ethanedithiol, 540-63-6.

Photocycloaddition Reactions of Norbornadiene and Quadricyclane with p-Benzoquinone

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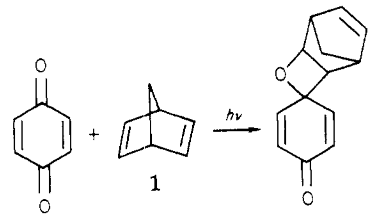
The photocycloaddition reactions of norbornadiene and its valence isomer quadricyclane with p-benzoquinone have been studied and compared. Irradiation of a solution of norbornadiene and p-benzoquinone in benzene yielded a mixture of the four isomeric 1:1 adducts **7**, **8**, **9**, and **10** in a ratio of ~48:16:21:15, respectively. Irradiation of a solution of quadricyclane and p-benzoquinone in benzene under similar conditions yielded a product mixture which consisted almost exclusively of the two exo adducts **7** and **8** in a ratio of ~56:44, along with traces of the endo adducts **9** and **10**. Chemical and spectroscopic evidence for the structures of the products is presented, and reaction pathways are proposed to account for their formation and for the different product distributions obtained from norbornadiene and quadricyclane.

Although photocycloaddition reactions of alkenes with carbonyl compounds have been extensively investigated,[1] only a few examples of reactions involving the photocycloaddition of a carbonyl compound to norbornadiene (**1**) have been described in the literature. In 1967 Bryce-Smith, Gilbert, and Johnson reported that the photoaddition of p-benzoquinone to norbornadiene gave the spirooxetane **2** in 22% yield as the only isolable product.[2] A few years later, Kubota, Shima, and Sakurai reported that irradiation of a solution of benzophenone and norbornadiene in benzene led to the formation of the adducts **3**, **4**, and **5** in yields of 32, 15, and 3%, respectively.[3] A kinetic study of the latter reaction subsequently revealed that these adducts actually resulted not from the addition of benzophenone to norbornadiene but from addition of the excited ketone to quadricyclane (**6**), generated in situ by benzophenone-sensitized photoisomerization of **1**.[4]



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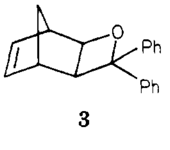

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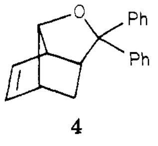

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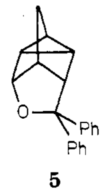

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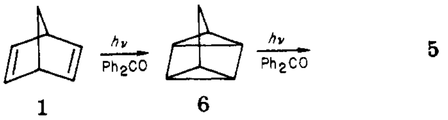

Consequently, the same cycloaddition products and the same product-distribution ratios were obtained when either norbornadiene or quadricyclane was irradiated in the presence of benzophenone under similar conditions.

Since efficient photosensitized isomerization of **1** to **6** requires sensitizers with triplet energies of at least 65–70 kcal mol^{-1} (e.g., benzophenone, $E_T \approx 69$ kcal mol^{-1}, and acetophenone, $E_T \approx 74$ kcal mol^{-1}),[5] p-benzoquinone ($E_T \approx 50$ kcal mol^{-1}) cannot serve effectively as a sensitizer for this photoisomerization. It seems likely, therefore, that adducts such as **2** formed in the irradiation of p-benzoquinone–norbornadiene mixtures result from the direct attack of quinone triplets on ground-state norbornadiene.[6] If this is true, it would be anticipated that different

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[1] See, for example: (a) D. O. Cowan and R. L. Drisko, "Elements of Organic Photochemistry", Plenum Press, New York, 1976, pp 181–93; (b) J. A. Barltrop and J. D. Coyle, "Excited States in Organic Chemistry", Wiley, New York, 1975, pp 208–18; (c) O. L. Chapman and G. Lenz, *Org. Photochem.*, 1, 283–321, (1967); (d) D. C. Neckers, "Mechanistic Organic Photochemistry", Reinhold, New York, 1967, pp 131–8.

[2] D. Bryce-Smith, A. Gilbert, and M. G. Johnson, *J. Chem. Soc. C*, 383 (1967).

[3] T. Kubota, K. Shima, and H. Sakurai, *Chem. Lett.*, 343 (1972).

[4] (a) A. A. Gorman and R. L. Leyland, *Tetrahedron Lett.*, 5345 (1972); (b) A. A. Gorman, R. L. Leyland, M. A. J. Rodgers, and P. G. Smith, *ibid.*, 5058 (1973).

[5] (a) G. S. Hammond, P. Wyatt, C. D. DeBoer, and N. J. Turro, *J. Am. Chem. Soc.*, **86**, 2532 (1964); (b) N. J. Turro, W. R. Cherry, M. F. Mirbach, and M. J. Mirbach, *ibid.*, **99**, 7388 (1977).

[6] For a discussion of the mechanism of oxetane formation in the photocycloaddition of p-benzoquinone to alkenes, see N. J. Bunce and M. Hadley, *Can. J. Chem.*, **53**, 3240 (1975).

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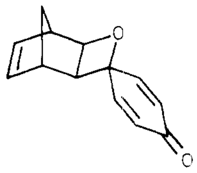
products or different product distributions might result from the photoaddition reactions of *p*-benzoquinone with norbornadiene and with quadricyclane.[7]

These considerations led us to investigate the photochemical behavior of mixtures of *p*-benzoquinone and quadricyclane and, for purposes of comparison, to reexamine the previously reported photocycloaddition reaction between *p*-benzoquinone and norbornadiene. Our observations show not only that different results are in fact obtained in the two cases but also that the photoaddition of *p*-benzoquinone to norbornadiene takes a somewhat more complicated course than was originally thought.

Irradiation of a solution of *p*-benzoquinone and norbornadiene in benzene under conditions similar to those used by the earlier investigators[2] gave a mixture containing four different 1:1 adducts, as determined by NMR and TLC analyses. Three of these compounds were isolated in pure form by column chromatography and have been assigned structures **7**, **8**, and **9** on the basis of their spectroscopic properties. The fourth isomer, which we have been unable to obtain completely free of compound **9**, has been tentatively identified on the basis of its NMR characteristics as the *endo*-oxetane **10**. NMR analyses of the crude reaction product mixture and of the fractions obtained from it during chromatographic separations of the components indicate that the original product mixture consisted of the four adducts **7**, **8**, **9**, and **10** in a ratio of approximately 48:16:21:15, respectively, along with small amounts of polymeric material.



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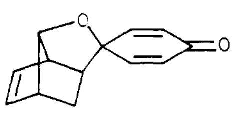

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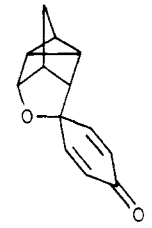

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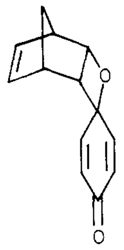

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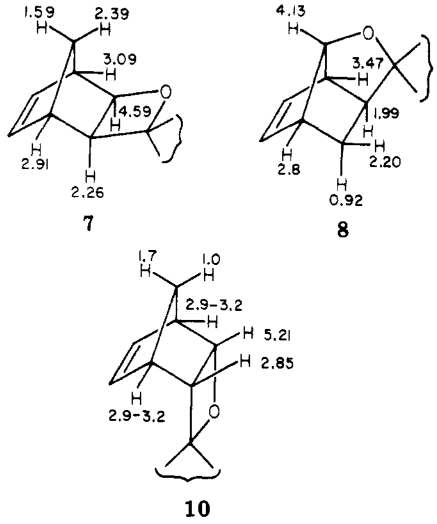
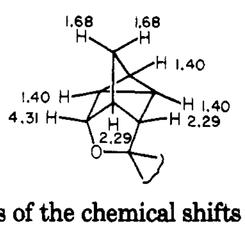
Irradiation of a benzene solution of *p*-benzoquinone and quadricyclane under similar conditions gave a product mixture which was found by TLC and NMR analyses to consist almost entirely of compounds **7** and **8** in a ratio of approximately 56:44, along with traces of the isomers **9** and **10** and small amounts of polymeric material. Repeated chromatographic separations of this mixture on silica gel and neutral alumina resulted in the isolation of pure samples of **7** and **8** which were identical with the corresponding products obtained in the photoaddition of *p*-benzoquinone to norbornadiene.

Chart I. Chemical Shift Assignments (δ)



All of the adducts show the spectroscopic characteristics of compounds containing the 2,5-cyclohexadienone moiety,[8] namely, prominent absorption bands in the 1660–1670, 1625–1635, and 855–865 cm^{-1} regions in their IR spectra and pairs of complex multiplets (each representing two protons) centered near δ 6 and 7 in their NMR spectra. The presence of an isolated CH═CH group in compounds **7**, **8**, and **10** is shown by additional NMR absorption in the δ 5.5–6.5 region due to another pair of vinylic protons. The NMR spectrum of compound **9**, on the other hand, displays only a well-resolved series of peaks with an integrated area equivalent to four protons in the δ 5.5–7 region, as would be expected for the assigned structure. The remainder of the 60-MHz spectrum of **9** is deceptively simple, consisting of four well-separated peaks which have the general appearance of broadened or distorted singlets but which, in the case of three of the peaks at least, were shown by spin-decoupling experiments to consist of overlapping multiplets with small coupling constants ($J \leq 3$ Hz). Thus, irradiation at δ 1.40 caused the peak at δ 4.31 to resolve into a clean doublet with $J = 3$ Hz, and irradiation at δ 2.29 caused the δ 4.31 peak to appear as a poorly resolved doublet with $J \approx 1$ Hz and the δ 1.40 peak to show evidence of fine structure. A comparison of these results with the NMR data reported for several related nortricyclane derivatives[9,10] leads us to propose the following chemical shift assignments (δ, CCl_4) for the protons in the nortricyclane moiety of **9**.



Our assignments of the chemical shifts for the nonvinylic protons in compounds **7**, **8**, and **10** are shown in Chart I.

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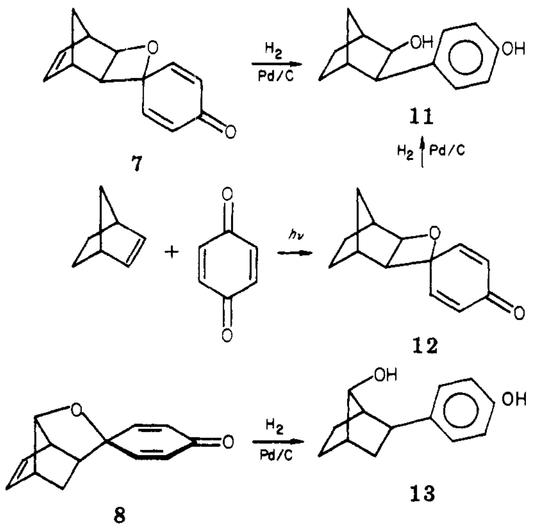
(7) Cf. T. Sasaki, K. Kanematsu, I. Ando, and O. Yamashita, *J. Am. Chem. Soc.*, **99**, 871 (1977). These workers report, in a paper which appeared while our work was in progress, that 9,10-phenanthrenequinone and acenaphthenequinone undergo photocycloaddition with norbornadiene to give only the corresponding *exo*-oxetanes (structures analogous to **3**) but that under similar conditions these quinones add to quadricyclane to give mixtures of the *exo*-oxetanes and the *exo*-oxolanes (structures analogous to **4**) in a ratio of 2:3.

(8) (a) F. G. Bordwell and K. M. Wellman, *J. Org. Chem.*, **28**, 2544 (1963); (b) K. L. Cook and A. J. Waring, *J. Chem. Soc., Perkin Trans. 1*, 529 (1973).

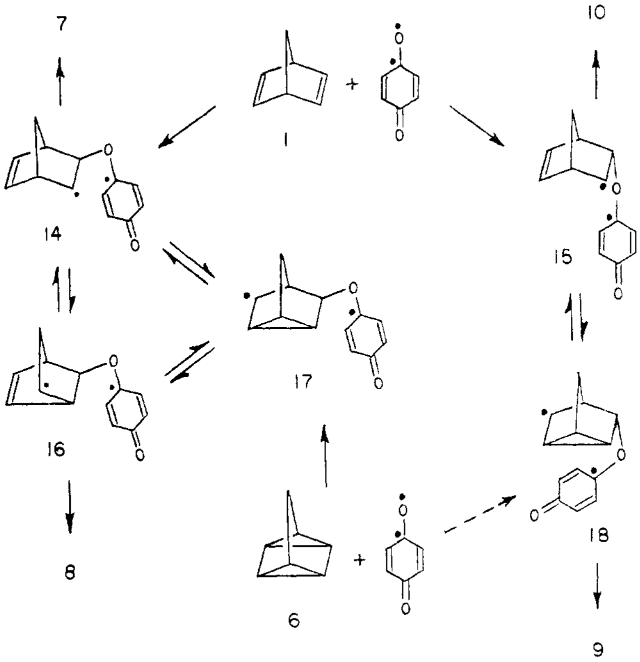
(9) (a) B. C. Henshaw, D. W. Rome, and B. L. Johnson, *Tetrahedron*, **27**, 2255 (1971), compound XXIII; (b) E. Crundwell and W. M. Kofi-Tsekpo, *ibid.*, **25**, 5535 (1969), compound III; (c) T. Kubota, K. Shima, and H. Sakurai, ref 3, compound III.

(10) In ref 9b, the assignment of the τ 7.42 (or 7.55) shift to H-2 in compound III (R = H) seems unreasonable; this shift should most likely be associated with H-3 (α to C═O). The confusion apparently arises from an error in numbering, since similar assignments are listed for H-2 in III (R = Me) and III (R = CH_2Br) in which C-2 is fully substituted.

Scheme I



Scheme II



These assignments are based on extensive spin-decoupling experiments and are consistent with spectroscopic observations reported in the literature for similar types of compounds. Thus, irradiation of the doublet (*J* = 9 Hz) at δ 1.59 in compound 7 caused the doublet (*J* = 9 Hz) at δ 2.39 to collapse to a singlet, in accord with expectations for the geminal bridge protons in the norbornene moiety.[11,12] Similarly, irradiation of the signal (doublet of doublets, *J* = 5 and 2 Hz) at δ 4.59, which can only be attributed to the proton α to the oxetane oxygen atom,[13] resulted in collapse of the doublet (*J* = 5 Hz) at δ 2.26, as would be expected for the signals arising from the protons occupying the 5- and 6-endo positions in the norbornene moiety.[14] The close resemblance between the upfield (δ <5) portions of the NMR spectra of 7 and those of other 5,6-disubstituted *exo*-norbornene derivatives,[11c] including another photoadduct of norbornadiene which has been identified as a norborneno-*exo*-oxetane,[7] provides additional support for the assigned structure.[15]

The results of spin-decoupling experiments on compound 8 were also in complete accord with the proposed structure and chemical shift assignments. Irradiation of the signal (doublet of doublets, *J* = 6 and 2 Hz) centered at δ 1.99 caused the doublet of doublets (*J* = 12 and 6 Hz) at δ 0.92 to collapse to a doublet (*J* = 12 Hz). Irradiation of the complex signal centered at δ 2.8 caused both the doublet of doublets (*J* = 12 and 5 Hz) at δ 2.20 and the triplet (*J* = 2 Hz) at δ 4.13 to collapse to doublets (*J* = 12 and 2 Hz, respectively). Irradiation of the multiplet at δ 3.47 caused both the doublet of doublets at δ 1.99 and the triplet at δ 4.13 to collapse to doublets (*J* = 6 and 2 Hz, respectively). Similar NMR results have been reported for the corresponding protons in other norbornene derivatives containing this type of oxolane ring.[3,7]

Compound 10 shows the expected downfield shift (Δδ ≈ 0.58–0.67)[11b,c] of its exo protons relative to the chemical shifts of the corresponding protons in the endo configuration in its stereoisomer 7. Unlike the situation with the exo-substituted norbornene 7, where one of the methylene bridge protons absorbs at unusually low field (δ 2.39), the syn and anti bridge-proton signals both appear at high-field positions (δ 1.7, 1.0) in the NMR spectrum of the endo-substituted isomer 10. These δ values are similar to those observed for the corresponding protons in norbornene and in substituted norbornenes which do not have highly anisotropic substituents in close proximity to the methylene bridge.[11,16]

Additional support for the structures assigned to 7 and 8 was provided by the chemical interconversions outlined in Scheme I. Catalytic hydrogenation of 7 in the presence of palladium/charcoal gave a phenol, $C_{13}H_{16}O_2$, which was shown (melting point, IR, NMR) to be identical with the compound obtained by reduction of the photoadduct from norbornene and *p*-benzoquinone. Since the predicted major product from the photoaddition of *p*-benzoquinone to norbornene is the *exo*-oxetane 12,[14] the phenol resulting from catalytic hydrogenation of this adduct should be

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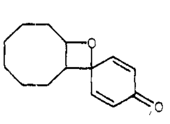
[11] (a) B. Franzus, W. C. Baird, Jr., N. F. Chamberlain, T. Hines, and E. I. Snyder, *J. Am. Chem. Soc.*, **90**, 3721 (1968); (b) A. P. Marchand and J. E. Rose, *ibid.*, **90**, 3724 (1968); (c) P. M. Subramanian, M. T. Emerson, and N. A. LeBel, *J. Org. Chem.*, **30**, 2624 (1965).

[12] Although the anti bridge proton absorbs at higher field than does the syn bridge proton in norbornene and in many substituted norbornenes,[11] we assign the lower field absorption to the anti bridge proton in 7 because of its closer proximity to the deshielding zone of the nearby cyclohexadienone system.

[13] Cf. D. R. Arnold, R. L. Hinman, and A. H. Glick, *Tetrahedron Lett.*, 1425 (1964), footnote d.

[14] R. R. Sauers, P. C. Valenti, and E. Tavss, *Tetrahedron Lett.*, 3129 (1975), and references cited therein.

[15] The NMR data reported by Bryce-Smith, Gilbert, and Johnson[2] for their product of the photoaddition of *p*-benzoquinone to norbornadiene are in good agreement with our data for compound 7, except for the inexplicable translocation of one proton from the region near δ 3 to the δ 1.4–1.7 region in the spectrum of the product obtained by the earlier workers. As grouped by these workers into six sets of "complex absorption" signals, the six regions of absorption are described as having relative areas (from low to high field) of 2:4:1:1:2:2, whereas our product gives relative areas of 2:4:1:2:2:1 for the corresponding grouping of signals. These workers also suggested, on the basis of similarities in the UV spectra of their norbornadiene–benzoquinone adduct and the cyclooctene–benzoquinone adduct i, that the norbornadiene adduct possessed the endo configuration, although the rationale leading to this conclusion was not explained.



i

[16] Inspection of scale models of the *exo*- and *endo*-oxetanes 7 and 10 clearly reveals the much greater distance between the cyclohexadienone moiety and the bridge protons in the endo isomer. It seems reasonable to assume, therefore, that the anti bridge proton in 10 absorbs at higher field than does the syn bridge proton, as has been found to be the case in other endo-substituted norbornenes.[11b,c]

expected to have structure **11**. The NMR spectra of compounds **11** and **12** are entirely consistent with the proposed structures (see Experimental Section). Analogously, catalytic hydrogenation of **8** afforded an isomeric phenol, the spectroscopic properties of which are in complete accord with those expected for structure **13**.

The formation of all of the observed adducts may be rationalized on the basis of a mechanism (Scheme II) involving equilibrating norbornenyl and nortricyclyl radicals, similar to the mechanisms proposed by Gorman and Leyland[4a] for the photocycloaddition of benzophenone to quadricyclane and by Kuivila and co-workers[17] for the free-radical addition reactions of norbornadiene. In contrast to the photochemical reactions of benzophenone with norbornadiene, in which triplet-sensitized isomerization of the diene to its highly strained valence isomer precedes the formation of biradical adducts, triplet *p*-benzoquinone appears to be able to add directly to either of these isomers to give initially different but interconvertible pairs of exo (**14**, **17**) and endo (**15**, **18**) biradical intermediates. Depending on the relative rates of interconversion ($\mathbf{14} \rightleftharpoons \mathbf{16} \rightleftharpoons \mathbf{17}$ and $\mathbf{15} \rightleftharpoons \mathbf{18}$) of these biradicals on the one hand and the rates at which they undergo spin inversion and ring closure on the other, product mixtures containing varying proportions of any or all of the isomeric adducts **7**, **8**, **9**, and **10** could be formed in these reactions. Thus, it is not surprising to find that the cycloaddition of *p*-benzoquinone to norbornadiene results in a much higher ratio of **7** to **8** than does the corresponding reaction with quadricyclane (3:1 vs. 1.3:1). The biradical **14** formed by exo attack of triplet *p*-benzoquinone on norbornadiene can be transformed directly into the *exo*-oxetane **7** by spin inversion and ring closure, whereas it must undergo at least one ($\mathbf{14} \rightarrow \mathbf{16}$) and possibly two ($\mathbf{14} \rightarrow \mathbf{17} \rightarrow \mathbf{16}$) rearrangements before cyclization to the *exo*-oxolane **8** can occur. In the exo addition of the triplet quinone to quadricyclane, however, ring closure is sterically impossible for the initially formed biradical **17**, which must first rearrange to **14** or **16** before it can cyclize to **7** and **8**, respectively. Perhaps the most notable difference in the photochemical behavior of these two hydrocarbons is the much higher degree of stereoselectivity observed in the reaction with quadricyclane, where virtually all of the product resulted from exo attack;[18] this may be compared with the norbornadiene reaction in which more than one-third of the product mixture must have resulted from endo attack. The unusually strong stereochemical preference of quadricyclane for exo addition has been noted by other investigators[4,7,19] and appears to be a general characteristic of both the thermal and the photochemical reactions of this interesting molecule.[20]

Experimental Section

Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 137 spectrophotometer calibrated against the 1601 cm^{-1} peak of polystyrene. Proton nuclear magnetic resonance spectra were recorded on a Hitachi Perkin-Elmer R-20B spectrometer, using tetramethylsilane as an internal standard. Elemental analyses were performed by Clark Microanalytical Laboratory. Irradiations were carried out in a cylindrical water-cooled borosilicate glass reaction vessel (Ace Glass) with a 200-W Hanovia medium-pressure mercury-vapor lamp fitted with a Kimax KG-33 filter sleeve (λ >300 nm). The progress of the photochemical reactions was monitored by TLC (silica gel; benzene–ethyl acetate, 9:1; UV visualization), irradiation being discontinued when *p*-benzoquinone could no longer be detected in the reaction mixture. Norbornadiene, norbornene, and spectrograde benzene (Aldrich) were used as received, and *p*-benzoquinone (Eastman Pract.) was recrystallized from hexane before use. Quadricyclane was prepared by the photoisomerization of norbornadiene[21] and was fractionally distilled under reduced pressure to remove traces of norbornadiene; the samples used showed no olefinic absorption in their NMR spectra.

Photocycloaddition of *p*-Benzoquinone to Norbornadiene. A solution of 2.0 g of *p*-benzoquinone and 35 mL of norbornadiene in 35 mL of benzene was irradiated under nitrogen for 2 h at room temperature. The reaction mixture was filtered to remove a small amount of insoluble polymeric material, and the filtrate was evaporated under vacuum on a rotary evaporator to provide 3.8 g of viscous yellow syrup. For NMR analysis, a small portion of this syrup was dissolved in CCl$_4$ and reevaporated under vacuum several times to remove traces of benzene and norbornadiene. Comparison of the NMR spectrum of the residue thus obtained with the spectra of the chromatographically separated components described below showed that it consisted almost entirely of a mixture of compounds **7**, **8**, **9**, and **10**. The crude product mixture was redissolved in benzene (10 mL) and chromatographed on a 2.5 × 55 cm column of silica gel (Mallinckrodt SilicAR CC-7) with C$_6$H$_6$–EtOAc (95:5) for development and elution. Fractions were monitored by TLC and NMR, and partially resolved fractions of similar composition were recombined and rechromatographed on silica gel or on Woelm neutral alumina; this process was repeated until sufficient separation of components was achieved to permit isolation of compounds **7**, **8**, and **9** in pure form. The order of elution of products on silica gel was $\mathbf{8} > \mathbf{7} > \mathbf{10} > \mathbf{9}$, with considerable overlapping of **7** with **8** and of **9** with **10**. NMR analysis of the partially separated products recovered from the first passage of the crude product through a silica gel column indicated that the adducts **7**, **8**, **9**, and **10** were present in the original reaction mixture in a ratio of approximately 48:16:21:15.

Compound **7** was obtained initially as a yellow oil; distillation in a Kugelrohr apparatus at 140–150 °C and 0.5 mm provided a middle fraction which slowly crystallized to a waxy solid. Recrystallization of this material from hexane gave colorless crystals: mp 64–65 °C; IR (melt) 3075, 2965, 1670, 1635, 1605, 1450, 1400, 1330, 1315, 1305, 1270, 1245, 1175, 1085, 975, 950, 935, 860, 845, 725, 700, 690 cm^{-1};[22] NMR (CDCl$_3$) δ 1.59 (1 H, d, J = 9 Hz), 2.26 (1 H, d, J = 5 Hz), 2.39 (1 H, d, J = 9 Hz), 2.91 (1 H, br s), 3.09 (1 H, br s), 4.59 (1 H, dd, J = 5 and 2 Hz), 5.70–6.25 (4 H, overlapping multiplets), 6.95–7.30 (2 H, m).

Anal. Calcd for C$_{13}$H$_{12}$O$_2$: C, 78.00; H, 6.04. Found: C, 77.82; H, 6.14.

Compound **8** was obtained as colorless crystals: mp 58.5–59.5 °C, after recrystallization from hexane; IR (melt) 3075, 2975, 1670, 1630, 1605, 1395, 1330, 1315, 1290, 1240, 1175, 1155, 1080, 1050, 1025, 980, 915, 875, 850, 790, 763, 743, 719, 699, 675 cm^{-1}; NMR (CCl$_4$) δ 0.92 (1 H, dd, J = 12 and 6 Hz), 1.99 (1 H, dd, J = 6 and

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[17] H. G. Kuivila, J. D. Kennedy, R. Y. Tien, I. J. Tyminski, F. L. Pelczar, and O. R. Khan, *J. Org. Chem.*, **36**, 2083 (1971).

[18] The traces of endo adducts **9** and **10** detected in the product mixture from the quadricyclane reaction may have resulted from side reactions involving small amounts of norbornadiene generated by photoisomerization of quadricyclane in the presence of the low-E_T quinone; see ref 5.

[19] (a) C. D. Smith, *J. Am. Chem. Soc.*, **88**, 4273 (1966); (b) N. Rieber, J. Alberts, J. A. Lipsky, and D. M. Lemal, *ibid.*, **91**, 5668 (1969); (c) G. Kaupp and H. Prinzbach, *Chem. Ber.*, **104**, 182 (1971); (d) I. Tabushi, K. Yamamura, and Z. Yoshida, *J. Am. Chem. Soc.*, **94**, 787 (1972); (e) W. Friedrichsen, E. Büldt, and R. Schmidt, *Tetrahedron Lett.*, 1137 (1975); (f) I. Tabushi, K. Yamamura, and A. Togashi, *J. Org. Chem.*, **41**, 2169 (1976).

[20] This does not apply, however, to transition-metal-catalyzed reactions of quadricyclane with electron-deficient olefins, which proceed via intermediate organometallic complexes and lead to endo derivatives of nortricyclane identical with those obtained in uncatalyzed 2,6-cycloaddition reactions ("homo-Diels–Alder reactions") of the same olefins with norbornadiene; see, for example, R. Noyori, I. Umeda, H. Kawauchi, and H. Takaya, *J. Am. Chem. Soc.*, **97**, 812 (1975).

[21] C. D. Smith, *Org. Synth.*, **51**, 133 (1971).

[22] These data are in good agreement with those reported by Bryce-Smith, Gilbert, and Johnson[2] for their product of this reaction, except for the *absence* of a strong absorption band in the 1010–1050-cm^{-1} region in the spectrum of our product. A particularly strong absorption band is present in this region, however, in the IR spectra of both **8** and **9**, and it also appeared in the spectra of our less highly purified samples of **7**, due to contamination with small amounts of one or both of these isomers.

2 Hz), 2.20 (1 H, dd, *J* = 12 and 6 Hz), 2.8 (1 H, m), 3.47 (1 H, m), 4.13 (1 H, distorted t, *J* = 2 Hz), 5.65 (1 H, ddd, *J* = 6, 3, and 2 Hz), 5.80–6.30 (3 H, overlapping multiplets), 6.80–7.25 (2 H, m).

Anal. Calcd for $C_{13}H_{12}O_2$: C, 78.00; H, 6.04. Found: C, 78.15; H, 6.04.

Compound **9** was obtained as colorless crystals: mp 105–106 °C, after recrystallization from cyclohexane; IR (Nujol) 1670, 1625, 1605, 1420, 1330, 1305, 1255, 1240, 1185, 1095, 1020, 955, 970, 930, 890, 865, 845, 820, 805 cm^{-1}; NMR (CCl_4) δ 1.40 (3 H, br s), 1.68 (2 H, s), 2.29 (2 H, narrow m), 4.31 (1 H, unresolved dd, *J* = 3 and 1 Hz), 5.87 (1 H, dd, *J* = 10 and 2 Hz), 6.01 (1 H, dd, *J* = 10 and 2 Hz), 6.57 (1 H, dd, *J* = 10 and 3 Hz), 6.90 (1 H, dd, *J* = 10 and 3 Hz).

Anal. Calcd for $C_{13}H_{12}O_2$: C, 78.00; H, 6.04. Found: C, 78.16; H, 6.05.

NMR analysis of the earlier eluted chromatographic fractions containing compound **9** revealed the presence of another component, which we were unable to isolate in pure form. The NMR spectrum of this compound, to which we have assigned structure **10**, was determined by subtracting the contribution made by **9** to the NMR spectrum of the mixture of **9** and **10**: NMR (CCl_4) δ 1.0 (1 H, d, *J* = 9 Hz), 1.7 (1 H, d, *J* = 9 Hz), 2.85 (1 H, t, *J* = 5 Hz), 2.9–3.2 (2 H, overlapping multiplets), 5.21 (1 H, t, *J* = 5 Hz), 5.7–6.0 (2 H, m), 6.1–6.5 (2 H, m), 6.8–7.3 (2 H, m).

Photocycloaddition of *p*-Benzoquinone to Quadricyclane. A solution of 2.0 g of *p*-benzoquinone and 35 mL of quadricyclane in 35 mL of benzene was irradiated for 7 h at room temperature. Removal of the solvent and unreacted quadricyclane under vacuum on a rotary evaporator provided 3.9 g of viscous yellow syrup, a small portion of which was dissolved in CCl_4 and reevaporated several times. NMR analysis of the residue showed that it consisted almost entirely of the adducts **7** and **8** in a ratio of approximately 56:44. Only traces of **9** and **10** could be detected in the NMR spectrum of this mixture. Chromatographic separation of the crude product mixture by the procedure described above provided samples of pure **7** and **8** which were identical (melting point, IR, NMR) with the corresponding compounds obtained in the *p*-benzoquinone–norbornadiene reaction.

Catalytic Hydrogenation of 7. A solution of **7** (91 mg) in 95% ethanol (10 mL) was hydrogenated at 45 psig of hydrogen in the presence of 10% palladium/charcoal (20 mg) for 1 h. After removal of the catalyst and solvent, the crude product was dissolved in 10 mL of 5% NaOH, and the solution was extracted with ether (2 × 5 mL) and acidified with dilute HCl. Extraction of the resultant mixture with ether (3 × 5 mL), followed by washing of the combined ether extracts with saturated NaCl, drying over Na_2SO_4, and evaporation, provided the phenol **11** (37 mg) as a microcrystalline white powder: mp 152–154 °C, after recrystallization from benzene;[23] IR (Nujol) 3350 (br), 1615, 1600, 1510, 1240, 1180, 1150, 1110, 1065, 1035, 840, 810, 789, 776, 724 cm^{-1}; NMR ($CDCl_3$–Me_2SO-d_6) δ 1.0–2.5 (8 H, m), 2.80 (1 H, d, *J* = 6 Hz, CHAr, endo), 3.85 (1 H, d, *J* = 6 Hz, CHOH, endo), 4.76 (2 H, br s, OH), 6.70 (2 H, d, *J* = 8 Hz, *o*-H in ArOH), 7.00 (2 H, d, *J* = 8 Hz, *m*-H in ArOH).

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.43; H, 7.89. Found: C, 76.22; H, 7.83.

Catalytic Hydrogenation of 8. A solution of **8** (210 mg) in 95% ethanol (20 mL) was hydrogenated at 45 psig of hydrogen in the presence of 10% palladium/charcoal (50 mg) for 1 h. The reaction mixture was worked up as described above, and the crude product was recrystallized from benzene to give the phenol **13** (132 mg) as colorless needles: mp 160–161 °C; IR (Nujol) 3300 (br), 1610, 1595, 1515, 1245, 1180, 1150, 1105, 1075, 840, 827, 722 cm^{-1}; NMR ($CDCl_3$–Me_2SO-d_6) δ 1.0–2.4 (8 H, m), 2.74 (1 H, d, *J* = 6 Hz, CHAr, endo), 3.97 (1 H, br s, CHOH), 5.36 (2 H, br s, OH), 6.70 (2 H, d, *J* = 8 Hz, *o*-H in ArOH), 7.17 (2 H, d, *J* = 8 Hz, *m*-H in ArOH).

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.43; H, 7.89. Found: C, 76.38; H, 7.68.

Photocycloaddition of *p*-Benzoquinone to Norbornene. A solution of 2.0 g of *p*-benzoquinone and 5.0 g of norbornene in 50 mL of benzene was irradiated under nitrogen for 5 h at room temperature. Solvent and unreacted norbornene were removed by rotary evaporation under vacuum to give 3.5 g of brown syrup. A portion (1.7 g) of this material was chromatographed once on a 2.5 × 55 cm column of silica gel with C_6H_6–EtOAc (95:5) to provide 0.59 g of the crude oxetane **12** as a yellow oil,[24] which was used in the following experiment without further purification.

Catalytic Hydrogenation of 12. A portion (156 mg) of the product obtained in the preceding experiment was dissolved in 95% ethanol (15 mL) and hydrogenated at 45 psig of hydrogen in the presence of 10% palladium/charcoal (50 mg) for 1 h. The reaction mixture was worked up as before, and the crude product (91 mg), mp 148–151 °C, was recrystallized from benzene to give a microcrystalline white powder, mp 151–153 °C, the IR and NMR spectra of which were identical with those of the product (**11**) obtained in the hydrogenation of **7**.

Registry No. 1, 121-46-0; **6**, 278-06-8; **7**, 72300-91-5; **8**, 72275-63-9; **9**, 72275-64-0; **10**, 72300-92-6; **11**, 72275-65-1; **12**, 72283-21-7; **13**, 72275-66-2; *p*-benzoquinone, 106-51-4.

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(23) The earlier workers[2] gave a melting point of 119–120 °C for the reduction product of their photoadduct.

(24) NMR analysis of this product indicated that it was a mixture of the exo and endo isomers in a ratio of ~4:1.

Asymmetric Reductions of α,β-Acetylenic Ketones and Acetophenone Using Lithium Aluminum Hydride Complexed with Optically Active 1,3-Amino Alcohols

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Asymmetric reduction of the α,β-acetylenic ketones **9a–f** using the freshly prepared complex derived from $LiAlH_4$ and (2*S*,3*R*)-(+)-4-(dimethylamino)-3-methyl-1,2-diphenyl-2-butanol (Darvon alcohol; **10**) at -70 °C gives mainly the (*R*)-carbinols **1a–f** in yields of 62–99% and enantiomeric excesses of 34–90%. Similar treatment of **9e** with the complex formed from $LiAlH_4$ and **11**, the enantiomer of **10**, affords **2e**, a useful intermediate for the synthesis of (2*R*,4′*R*,8′*R*)-α-tocopherol (vitamin E), in 96% yield and 90% ee. The optically pure 1,3-amino alcohol ligands **12–16**, which are structurally related to **10**, were prepared by starting from the known (*S*)-ether sulfonate **23** and its enantiomer. Reduction of **9a** and acetophenone using the $LiAlH_4$–**12** complex gives an excess of the corresponding (*S*)-carbinols **2a** (36% ee) and **27** (60% ee), respectively.

The optically active acetylenic carbinols **1a,b,d,e** and **2a,b,d,e** (Scheme I, Table I) are key intermediates in certain recently developed approaches to the total synthesis of (2*R*,4′*R*,8′*R*)-α-tocopherol (vitamin E) and related