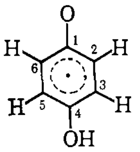
Table III. Hyperfine Coupling Constants for Benzosemiquinone Radical in Ethers[a]



$\alpha_{H_3} = 5.5$ gauss
$\alpha_{H_5} = 5.5$ gauss
$\alpha_{H(-OH)} = 1.5$ gauss
$\alpha_{H_2} = 0.75$ gauss
$\alpha_{H_6} = 0.75$ gauss

[a] See text for justification of assignments.

Inasmuch as porphyrins can function either as one-electron reductants[2] or as one-electron oxidants,[5,16,17] it is important to ask whether the same excited state is involved in both processes. Fujimori and Tavla[17] have shown that β-carotene, a specific quencher of the chlorophyll triplet, is capable of preventing the chlorophyll-sensitized photoxidation of hydroquinone. We have confirmed this and have also shown that β-carotene can quench the chlorophyll-sensitized reduction of *p*-benzoquinone (Figure 7). From these data, one can calculate a Stern–Volmer quenching constant of 4×10^4 M^{-1}. From the data of Fujimori and Tavla,[17] a quenching constant of 2.5×10^4 M^{-1} can be calculated. These are in satisfactory agreement, considering the difficulties inherent in the measurements. We can thus conclude that the chlorophyll triplet can indeed function in both types of redox processes. One can visualize this in terms of the diagram in Figure 8. Perhaps this has significance for the functioning of chlorophyll in the two photochemical systems of photosynthesis.[18]

(16) E. Fujimori and M. Tavla, *Nature*, **208**, 78 (1965).

(17) E. Fujimori and M. Tavla, private communication.

(18) NOTE ADDED IN PROOF. Recently, Gough (*Trans. Faraday Soc.*, 62, 2321 (1966)) has observed the epr spectrum of the monoprotonated *p*-benzosemiquinone species, produced by ultraviolet irradiation, in a variety of organic solvents. An 18-line spectrum was observed, probably analogous to the spectrum shown in Figure 6 of the present work, although better resolved. The coupling constants are quite similar to those given in Table III above. In addition, evidence for hydrogen bonding of the hydroxyl hydrogen to the solvent is presented.

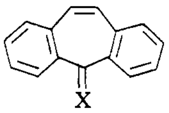
Communications to the Editor

The Stereospecific Addition of Dibenzo[*a*,*d*]cycloheptenylidene and Tribenzo[*a*,*c*,*e*]cycloheptenylidene to Olefins

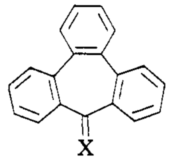
Sir:

It is known that carbenes substituted by aryl groups add to olefins in a nonstereospecific manner; this has been attributed to the triplet nature of the intermediate involved.[1-3] Thus Skell's hypothesis for the stereochemical course in addition reactions seems still to be valid in spite of the recent criticisms cited in the literatures.[4,5]

We wish to report that aryl-substituted carbenes, *i.e.*, dibenzo[*a*,*d*]cycloheptenylidene (**1a**) and tribenzo[*a*,*c*,*e*]cycloheptenylidene (**2a**), add to *cis*- and *trans*-2-butenes stereospecifically.[6] The ground-state triplet nature of **1a** and **2a** is clearly shown by electron spin resonance studies.[7]



1a, X = :
b, X = O
c, X = $NNHSO_2C_6H_4CH_3$
d, X = N_2



2a, X = :
b, X = O
c, X = $NNHSO_2C_6H_4CH_3$
d, X = N_2

p-Toluenesulfonylhydrazones **1c**, mp 204° dec, and **2c**, mp 213° dec, are obtained from the corresponding ketones **1b**[8] and **2b**,[9] respectively. The reaction of these hydrazones with sodium methoxide in dry pyridine affords the diazo compounds 5-diazodibenzo[*a*,*d*]cycloheptene (**1d**), mp 62° dec (25% yield), and 9-diazotribenzo[*a*,*c*,*e*]cycloheptene (**2d**), mp ~60° dec (4% yield).

The diazo compounds **1d** and **2d** were irradiated in *cis*- and *trans*-2-butenes at 0° with a 1000-w high-pressure mercury lamp.[10] Stereospecific addition of **1a** was confirmed on the following basis. No *trans*-2,3-dimethylcyclopropane derivative was detected during the photolysis of **1a** in *cis*-2-butene. The hydrocarbon fraction obtained was subjected to alumina chromatography and divided into *ca.* 50 fractions. Each fraction was checked by infrared spectroscopy. No sign of the existence of the *trans* isomer was detected. Moreover, the crude hydrocarbon fraction was analyzed by vpc,[11] and no peak corresponding to the *trans* isomer was detected.

---

(1) R. M. Etter, H. S. Skovronek, and P. S. Skell, *J. Am. Chem. Soc.*, 81, 1008 (1959).

(2) (a) G. L. Closs and L. E. Closs, *Angew. Chem.*, **74**, 431 (1962); (b) E. Funakubo, I. Moritani, T. Nagai, S. Nishida, and S. Murahashi, *Tetrahedron Letters*, 1069 (1963); (c) C. D. Gutsche, G. L. Backman, and R. S. Coffey, *Tetrahedron*, **18**, 617 (1962); (d) P. S. Skell and J. Klebe, *J. Am. Chem. Soc.*, **82**, 247 (1960).

(3) M. Jones, Jr., and K. R. Rettig, *ibid.*, **87**, 4013, 4105 (1965).

(4) W. B. DeMore and S. B. Benson, *Advan. Photochem.*, **2**, 219 (1964).

(5) P. P. Gaspard and G. S. Hammond, "Carbene Chemistry," W. Kirmse, Ed., Academic Press Inc., New York, N. Y., 1964, p 235.

(6) The addition of phenylcarbene to 2-butene is not completely stereospecific; the product from *cis*-2-butene was contaminated with 2.5% 3-phenyl-*trans*-1,2-dimethylcyclopropane.[2c]

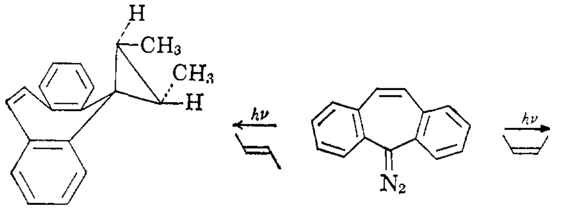
(7) I. Moritani, S. Murahashi, M. Nishino, Y. Yamanoto, K. Itoh, and N. Mataga, *J. Am. Chem. Soc.*, **89**, 1259 (1967).

(8) (a) W. Treibs and H.-J. Klinkhammer, *Chem. Ber.*, **84**, 671 (1951); (b) T. W. Campbell, R. Ginsig, and H. Schmid, *Helv. Chim. Acta*, **36**, 1489 (1953).

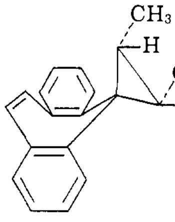
(9) W. Tochterman, K. Oppenländer, and U. Walter, *Chem. Ber.*, **97**, 1329 (1964).

(10) Halos POH 1000 Eikosha Co. Ltd., Osaka, Japan.

(11) The crude hydrocarbon fraction was analyzed by vpc (Apieson L, 2 m, at 240°). No isomerization and decomposition was observed in this condition.



4 **1d**

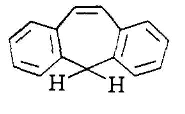


3

Irradiation of a solution of **1d** in *cis*-2-butene affords *cis*-2,3-dimethylspiro[cyclopropane-1,5′-(dibenzo-[*a*,*d*]cycloheptene)] (**3**) in 11% yield, mp 60.5–61.5°. *Anal.* Calcd for $C_{19}H_{18}$: C, 92.63; H, 7.73. Found: C, 92.59; H, 7.54. Compounds **3** and **4** are shown to be isomeric by mass spectrometry (*m*/*e* 246, common to both). Compound **3** shows maxima at λ (EtOH) 214 mμ (log ε 4.5) and 285 mμ (log ε 4.1). The nmr spectrum consists of doublets at τ 8.70 and 9.54 (J = 7 cps, methyl protons) and multiplets at τ 8.0–8.3 and 9.2–9.5 (cyclopropyl protons). This result shows that inversion of the conformation of the nonplanar ring in compound **3** is difficult,[12] although inversion of tropylidene is very fast.[13] This can be interpreted in terms of steric repulsion between the hydrogen atoms of the benzene rings and that of methyl groups in a planar transition state. Thus, the methyl protons H^a and cyclopropyl proton H^b are deshielded by the anisotropy of both benzene rings.

Irradiation of a solution of **1d** in *trans*-2-butene gives the *trans* isomer of **3** (**4**) in 2% yield, mp 59–60°, *m*/*e* 246, $\lambda_{\max}^{\text{EtOH}}$ 214 mμ (log ε 4.2) and 285 mμ (log ε 3.8), nmr methyl protons at τ 8.58 and 9.40 and cyclopropyl protons at τ 8.5–8.65 and 9.35–9.5. *Anal.* Found: C, 92.40; H, 7.29.

Photolysis of **1d** in *cis*-2-butene gives the cyclopropane derivative **3**, dimer **8** (mp 334°, 23% yield),[14] ketazine **9** (mp 226–226.5°, 9%),[14] and hydrogen abstraction products[11] **5** (2%), **6** (2%), and **7** (2%). Dibenzo[*a*,*d*]cycloheptene (**5**, mp 92°) was confirmed by comparison with an authentic sample.[8a] The structures of *cis*-4-(dibenzo[*a*,*d*]cyclohepten-5-yl)-2-butene (**6**)[14] and 3-(dibenzo[*a*,*d*]cyclohepten-5-yl)-1-butene (**7**)[14] were assigned by nmr.[15]



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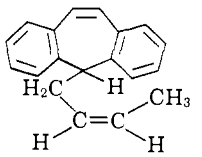

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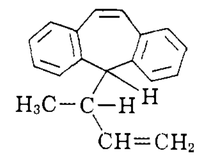

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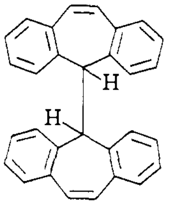

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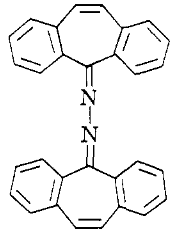
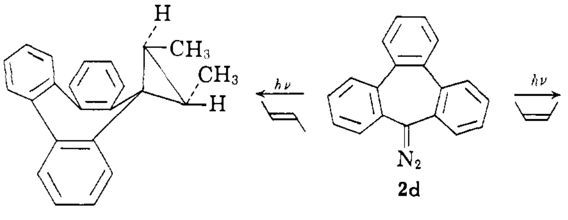
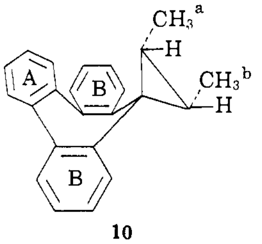


9

Irradiation of a solution of **2d** in *cis*-2-butene yields *cis*-2,3-dimethylspiro[cyclopropane-1,9′-(tribenzo[*a*,*c*,*e*]cycloheptene)] (**10**) in 70% yield,[16] mp 158–159°. *Anal.* Calcd for $C_{23}H_{20}$: C, 93.20; H, 6.80. Found: C, 93.40; H, 6.75. Compounds **10** and **11** were also shown to be isomeric by mass spectrometry (*m*/*e* 296, common to both). Compound **10** shows maxima at λ (EtOH) 230 mμ (log ε 5.1), 240 (sh), and 260 (sh). The nmr spectrum consists of doublets at τ 8.77 and 9.80 (J = 6.5 cps, methyl protons) and multiplets at τ 8.15–8.40 and 9.35–9.60 (cyclopropyl protons). The energy barrier to ring inversion of tribenzo[*a*,*c*,*e*]cycloheptene is high.[17] Thus, the methyl protons H^a of **10** (τ 9.80) are strongly shielded by benzene ring A, while the methyl protons H^b (τ 8.77) are deshielded by benzene rings B.



11 **2d**



10

On the other hand, irradiation of a solution of **2d** in *trans*-2-butene gives the *trans* isomer of **10** (**11**) in 29% yield, mp 112–112.5°, *m*/*e* 296, $\lambda_{\max}^{\text{EtOH}}$ 230 mμ (log ε 4.7), 240 (sh), and 260 (sh), methyl protons at τ 8.62 and 9.75 and cyclopropyl protons at τ 8.55–8.8 and 9.7–9.85. *Anal.* Found: C, 93.06; H, 6.80. A dimer **12** (mp 384°),[14] corresponding to **8**, is also obtained in 2% yield.

Thus it is clear that the addition of carbenes **1a** and **2a** to 2-butene proceeds stereospecifically.[18] This

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(12) Although ring inversion of 10-bromodibenzo[*a*,*d*]cyclohepten-5-one dimethyl acetal was observed (W. Tochtermann, U. Walter, and A. Mannschreck, *Tetrahedron Letters*, 2981 (1964), ring inversion of **3** was not observed at 170°.

(13) (a) F. A. L. Anet, *J. Am. Chem. Soc.*, 86, 458 (1964); (b) F. R. Jensen and L. A. Smith, *ibid.*, 86, 956 (1964).

(14) Satisfactory elemental analytical data and ultraviolet and infrared spectra have been obtained for this compound.

(15) In the nmr spectrum of **6**, the methyl protons appear as a doublet at τ 8.66 (J = 5 cps), the methylene protons as a multiplet at τ 7.5–7.65, the methine proton as a triplet at τ 6.17 (J = 6 cps), and the vinyl protons as a multiplet at τ 4.6–5.0. In the nmr spectrum of **7**, the methyl protons appear as a doublet at τ 9.35 (J = 7 cps), the benzyl methine proton as a doublet at τ 6.47 (J = 10 cps), the allyl methine proton as a multiplet at τ 7.0–7.3, and the vinyl protons as a multiplet at τ 4.6–5.6.

(16) The cyclopropane fraction was precisely checked by nmr and no peak for the *trans* isomer was observed.

(17) The energy barrier to ring inversion of 9-carboxymethylene-tribenzo[*a*,*c*,*e*]cycloheptene is so high ($\Delta F^{\ddagger}$ = 31 kcal/mole at 139°) that this compound can be resolved (W. Tochterman and H. Küppers, *Angew. Chem.*, 77, 173 (1963)).

(18) Although pyrazolines are known to decompose upon irradiation in a stereospecific fashion,[19] the formation of pyrazoline followed by decomposition to the cyclopropane derivative was rejected by the fact that no pyrazoline was obtained from the reaction of diazo com-

stereospecific addition could be easily explained by assuming that all addition proceeds through the singlet state while hydrogen abstraction is a triplet-state reaction,[20] since stereospecific addition is usually interpreted in terms of singlet-state reaction. This is in agreement with a triplet ground state as it is well known that methylene addition in solution is stereospecific although methylene also has a triplet ground state.[21]

Another explanation might be advanced. The hydrogen abstraction products, **5–8** and **12**, are obtained together with the addition products. This result strongly suggests that a considerable amount of triplet state is involved in these reactions. This triplet carbene may possibly add to olefin to give cyclopropane as well as other arylcarbenes.[1–3] Since the present results show the stereospecific addition, triplet carbene might add to olefin stereospecifically.

pounds **1d** and **2d** with 2-butene, and abstraction products, **5–8** and **12**, were obtained.

(19) T. V. Van Auken and K. L. Rinehart, Jr., *J. Am. Chem. Soc.*, **84**, 3736 (1962).

(20) (a) H. E. Zimmerman and D. H. Paskovich, *ibid.*, **86**, 2149 (1964); (b) V. Franzen and H. I. Joschek, *Ann.*, **633**, 7 (1960); (c) W. Kirmse, L. Horner, and H. Hoffmann, *ibid.*, **614**, 19 (1958); (d) E. Ciganek, *J. Am. Chem. Soc.*, **88**, 1979 (1966); (e) D. M. Gale, W. J. Middleton, and C. G. Krespan, *ibid.*, **88**, 3617 (1966).

(21) Reference 5, Chapter 2, p 7.

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Received November 21, 1966

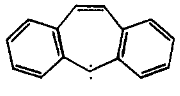
The Electron Spin Resonance of Triplet Dihydrodibenzo[*a*,*d*]cycloheptenylidene, Dibenzo[*a*,*d*]cycloheptenylidene, and Tribenzo[*a*,*c*,*e*]cycloheptenylidene

Sir:

In the preceding communication[1] we reported that dibenzo[*a*,*d*]cycloheptenylidene (**1**) and tribenzo[*a*,*c*,*e*]cycloheptenylidene (**2**) added to olefins stereospecifically to give cyclopropanes. Generally, carbenes which have a π-benzene system next to the divalent carbon show ground-state triplet and would add to olefins in a nonstereospecific fashion.[2,3] It is interesting to know whether the ground state of **1** or **2** is a triplet or not. Dihydrodibenzo[*a*,*d*]cycloheptenylidene (**3**) was also investigated and compared with **1**, **2**, and diphenylmethylene (**4**).

These carbenes (**1–3**) showed a triplet ground state. The corresponding diazo compounds were irradiated with ultraviolet light of wavelength below 3000 A at 77°K. The spectra were obtained with a Japan Electron Optics Lab JES-3BX spectrometer with 100-kc field modulation, and showed characteristics of randomly oriented triplets of low symmetry. The spectra persisted for hours after irradiation ceased, indicating that the observed species were in the ground states.

The spectra can be described by the Hamiltonian[4]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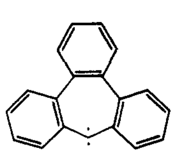
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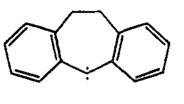
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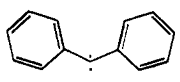
4

$$\mathcal{H} = g\beta\vec{H}\vec{S} + DS_{z2} + E(S_{x2} - S_{y2})$$

where $S = 1$. The zero-field parameters obtained from these observations were: for **1**, $D = 0.3787$ cm^{-1}, $E = 0.0162$ cm^{-1}; for **2**, $D = 0.4216$ cm^{-1}, $E = 0.0195$ cm^{-1}; and for **3**, $D = 0.3932$ cm^{-1}, $E = 0.0170$ cm^{-1}. The larger D value observed, compared to that of the phosphorescent triplet state of the aromatic hydrocarbons, requires a significant one-center interaction and indicates one unpaired electron largely localized in an n orbital at C-1, the divalent carbon atom, and another delocalized in a π orbital.

It is interesting to compare carbene **3** with diphenylmethylene (**4**; $D = 0.405$ cm^{-1}, $E = 0.019$ cm^{-1}).[5–9] The nonzero value of E for **4** eliminates[5] a structure of D_{2d} symmetry[3] (the aromatic rings are perpendicular to each other and bound to the central carbon). The angle between the axes of the C-1 hybrids for **4** and phenylcarbene were calculated to be ~150°,[10] a value supported by the examination of the ^{13}C hyperfine splittings.[11] For **3**, the value of E/D is similar to that of diphenylmethylene, so the angle formed by the axes of the hybrids at C-1 appears to be ~150°. This value is greater than the internuclear angle of the seven-membered ring, which is presumably due to the fact that the bonds to C-1 in **3** are bent bonds.[6,11]

If the C-1 hybrids of **3** are sp^2, similar to ketone, it is clear that the π orbital on C-1 is almost perpendicular to the π orbitals of both benzene rings. Such a model is clearly inconsistent with the observed D value. On the other hand, the enlargement of the angle of the axes of the hybrids at C-1 increases the s character of the bonds of the carbon and the planarity of the seven-membered ring, which contributes to the delocalization of the π electron of the C-1 atom with both benzene rings. The above consideration also suggests the bent bond of C-1 in **3**.

The D value for **3** is smaller than that of **4**. Greater opportunity for π delocalization should reduce the density of the π electron on the C-1 atom, and, thus, reduce the value of D. Recently we reported the ab-

(1) S. Murahashi, M. Nishino, and I. Moritani, *J. Am. Chem. Soc.*, **89**, 1257 (1967).

(2) (a) G. L. Closs and L. E. Closs, *Angew. Chem.*, **74**, 431 (1962); (b) E. Funakubo, I. Moritani, T. Nagai, S. Nishida, and S. Murahashi, *Tetrahedron Letters*, 1069 (1963); (c) M. Jones, Jr., and K. R. Rettig, *J. Am. Chem. Soc.*, **87**, 4013, 4015 (1965); (d) C. D. Gutsche, G. L. Backman, and R. S. Coffey, *Tetrahedron*, **18**, 617 (1962); (e) P. S. Skell and J. Klebe, *J. Am. Chem. Soc.*, **82**, 247 (1960); (f) E. Ciganek, *ibid.*, **88**, 1979 (1966); (g) D. M. Gale, W. J. Middleton, and C. G. Krespan, *ibid.*, **88**, 3617 (1966).

(3) R. M. Etter, H. S. Skovronek, and P. S. Skell, *ibid.*, **81**, 1008 (1959).

(4) K. W. H. Stevens, *Proc. Roy. Soc.* (London), **A214**, 235 (1952).

(5) R. W. Murray, A. M. Trozzolo, E. Wasserman, and W. A. Yager, *J. Am. Chem. Soc.*, **84**, 3213 (1962).

(6) R. W. Brandon, G. L. Closs, and C. A. Hutchinson, Jr., *J. Chem. Phys.*, **37**, 1878 (1962).

(7) E. Wasserman, A. M. Trozzolo, W. A. Yager, and R. W. Murray, *ibid.*, **40**, 2408 (1964).

(8) E. Wasserman, L. C. Snyder, and W. A. Yager, *ibid.*, **41**, 1763 (1964).

(9) R. W. Brandon, G. L. Closs, C. E. Davoust, C. A. Hutchinson, Jr., B. E. Kohler, and R. Silbey, *ibid.*, **43**, 2006 (1965).

(10) J. Higuchi, *ibid.*, **39**, 1339 (1963).

(11) E. Wasserman, L. Barash, A. M. Trozzolo, R. W. Murray, and W. A. Yager, *J. Am. Chem. Soc.*, **86**, 2304 (1964).