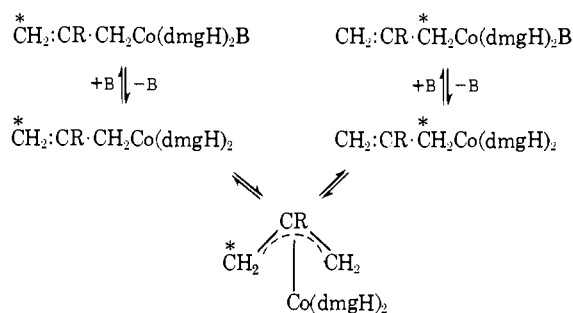


are accompanied by an upfield shift and marked broadening of the residual solvent hydroxyl resonance and by a broadening and disappearance of the bridging hydroxyl resonance of the equatorial dioximato ligands at  $\delta$  18.6 (not shown in the figure).

The reversible changes in the character of the axial ligand resonances which accompany the reversible changes in the character of the allyl and 2-methylallyl proton resonances clearly indicate that the dynamic character of the allyl group is closely associated with axial ligand exchange. Five-coordinate organocobaloximes are believed to be transient intermediates in such ligand exchanges,<sup>8</sup> but attempts to obtain stable five-coordinate species have shown that, even in non-coordinating solvents in the absence of suitable axial ligands, an oxygen of an equatorial dioximato ligand of one molecule prefers to act as an axial ligand of a second molecule thus maintaining six-coordination.<sup>9</sup> We therefore ascribe the formation of the dynamic  $\sigma$ -allylcobaloximes to the fact that transient intermediate five-coordinate allyl complexes can adopt the  $\pi$ -allyl configuration, even though the relatively inflexible dioximato equatorial ligands ensure that six-coordinate  $\sigma$ -allyl complexes predominate in solution, the rate of the dynamic exchange being dependent upon the rate of formation of the five-coordinate species. (See Scheme I.)

Scheme I



(dmgH)<sub>2</sub> = conjugate base of dimethylglyoxime;

B = axial ligand

Thus, with a weakly coordinating axial ligand such as water,<sup>10</sup> the rate of formation and the proportion of the five-coordinate species are large. With a more strongly bound axial ligand, such as pyridine, the rates of formation and proportion of the five-coordinate species are appreciably smaller and may be reduced still further by the addition of an excess of that ligand.

These observations contrast with those for the more flexible allyl-<sup>11</sup> and 3-methylallyltetracyanocobaltate-(III)<sup>12,13</sup> ions, which clearly demonstrate that the latter complexes have  $\pi$ -allyl character in D<sub>2</sub>O and revert to six-coordinate  $\sigma$ -allyl complexes on addition of an excess of cyanide ion.

(8) (a) Reference 1a, pp 42–51; (b) T. Sakurai, J. P. Fox, and L. L. Ingraham, *Inorg. Chem.*, **10**, 1105 (1971); (c) A. L. Crumbliss and W. K. Wilmarth, *J. Amer. Chem. Soc.*, **92**, 2593 (1970); (d) J. Halpern and D. N. Hague, *Inorg. Chem.*, **6**, 2059 (1967); (e) K. L. Brown and R. G. Kallen, *J. Amer. Chem. Soc.*, **94**, 1894 (1972).

(9) T. L. Brown, L. M. Ludwick, and R. S. Stewart, *J. Amer. Chem. Soc.*, **94**, 384 (1972).

(10) References 8b, c, and e.

(11) J. Kwiatek and J. K. Seyler, *J. Organometal. Chem.*, **3**, 421 (1965).

(12) T. Funabiki and K. Tarama, *Chem. Commun.*, 1177 (1971).

(13) 3-Methylallylcobaloxime and other unsymmetrical substituted allylcobaloximes show characteristic  $\sigma$ -allyl spectra under all the conditions described above.

Though the exact configuration of the five-coordinate allyl complexes is not known, these results demonstrate the relative ease with which the dioximato ligands may allow attack of a reagent cis to the organic ligand. In particular, it is interesting that oxygen insertion reactions of allylcobaloximes are very rapid under conditions in which the five-coordinate allyl complex is formed and may be suppressed by the addition of ligands which induce formation of the six-coordinate complex.<sup>14</sup> The 2-methylallylcobaloximes, which have not previously been described and which show the most pronounced dynamic character, are also especially prone to thermal reaction with oxygen.

**Acknowledgment.** We thank the Science Research Council for financial support.

(14) C. Merienne, C. Giannotti, and A. Gaudemer, *J. Organometal. Chem.*, **54**, 281 (1973).

David Dodd, Michael D. Johnson\*

Department of Chemistry, University College London  
London WC1H 0AJ, England

Received November 16, 1973

### An Unusual Case of Selectivity in a Photochemical Reaction. Photoisomerization of Unsymmetrical 1,3-Dienes

Sir:

Two major questions concerning photochemical reactions where multiple pathways exist are those of selectivity and the factors governing selectivity where observed. A case where these questions apply is photoisomerization phenomena of dienes and polyenes. Studies to date have been limited mostly to relatively simple alkyl-substituted systems.<sup>1–5</sup> For these systems relatively little selectivity is observed; most isomerization phenomena for dienes can be accounted for in terms of equilibrating allyl methylene intermediates for triplet states<sup>1–3</sup> and nonequilibrating allyl methylene intermediates for singlets.<sup>5</sup> Intersystem crossing is unimportant in most systems investigated.<sup>1–3,5</sup> For the few trienes and polyenes studied,<sup>2,4</sup> little preference has been found as to the site—central or terminal bond—of isomerization.<sup>2a</sup> The present paper reports a study of isomerization phenomena of an unsymmetrical diene, 1-(4-pyridyl)-4-phenylbutadiene. Rather surprisingly this diene exhibits high selectivity in photoisomerization which can best be explained in terms of rapid or selective radiationless decay from one of several equilibrating species.

1-(4-Pyridyl)-4-phenyl-*trans*-1, *trans*-3-butadiene (1) and 1-(4-pyridyl)-4-phenyl-*trans*-1, *cis*-3-butadiene (2) were prepared by a Wittig condensation of benzyltriphenylphosphonium bromide with 3-(4-pyridyl)acrolein.<sup>6,7</sup> The product mixture (~60% 2) was separated

(1) J. Saltiel, J. D'Agostino, E. D. Megarity, L. Metts, K. R. Neuberger, M. Wrighton, and O. C. Zafriou, *Org. Photochem.*, **3**, 1 (1973).

(2) (a) R. S. H. Liu and Y. Butt, *J. Amer. Chem. Soc.*, **93**, 1532 (1971); (b) R. S. H. Liu, *Pure Appl. Chem., Suppl.*, **1**, 335 (1971).

(3) (a) J. Saltiel, D. E. Townsend, and A. Sykes, *J. Amer. Chem. Soc.*, **95**, 5968 (1973); (b) J. Saltiel, A. D. Rousseau, and A. Sykes, *ibid.*, **94**, 5903 (1972); (c) J. Saltiel, L. Metts, and M. Wrighton, *ibid.*, **91**, 5684 (1969).

(4) K. J. Crowley, *J. Org. Chem.*, **33**, 3679 (1968).

(5) J. Saltiel, L. Metts, and M. Wrighton, *J. Amer. Chem. Soc.*, **92**, 3227 (1970).

(6) R. N. McDonald and T. W. Campbell, *Org. Syn.*, **40**, 36 (1960).

(7) S. Trippett and D. M. Walker, *J. Chem. Soc.*, 1266 (1961).

by fractional crystallization to yield pure samples of **1** and **2**. 1-(4-Pyridyl)-4-phenyl-*cis*-1,*trans*-3-butadiene (**3**) and **1** were prepared and purified by an analogous procedure from cinnamyltriphenylphosphonium chloride and 4-pyridylcarboxaldehyde. The *trans,trans* **4** and *cis,trans* **5** isomers of 1,4-diphenyl-1,3-butadiene were prepared by a similar procedure.<sup>6</sup>

Irradiation of **1** in degassed benzene solution over the wavelength range 300–400 nm was found to lead almost exclusively to **3**.<sup>8</sup> The isosbestic point at 305 nm was maintained well past attainment of the photostationary state and only after a total dose of *ca.* ten times that required to reach the stationary state could any other products—but no **2**—be detected by vpc. Quantum yields for the conversion of **1** to **3** were found to be 0.30 at both 313 and 366 nm; from photostationary states of 78% **3** at 366 nm and 60% **3** at 313 nm and the extinction coefficients of **1** and **3** at these wavelengths, the quantum yield from **3** to **1** was calculated to be 0.24 and 0.23 at 366 and 313 nm, respectively.

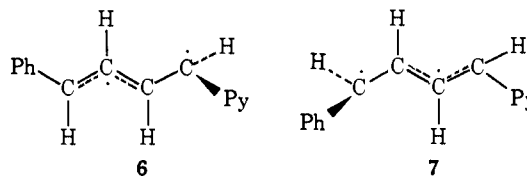
In contrast to the results obtained with **1**, irradiation of **4** led first to formation of **5** and subsequently to a new product having a shorter vpc retention time, presumably the *cis,cis* isomer.<sup>9,10</sup> Isosbestic points were not maintained after the initial phase of the reaction; however, approximate stationary states between **4** and **5** of 64% **5** at 366 nm and 60% **5** at 313 nm were obtained (about 1–2% *cis,cis* isomer in each case). Quantum yields for conversion of **4** to **5** and the reverse are 0.25 and 0.19, respectively.

Irradiation of solutions of **2**, the *cis,trans* isomer not formed upon direct irradiation of **1**, led only to **1** and **3**. The quantum yield for formation of **1** from **2** was 0.07.<sup>11</sup> No additional products were detected even on prolonged irradiation.

Irradiation of benzene solutions of **1** with sensitizers such as benzophenone, Michler's ketone, and biacetyl resulted in no detectable sensitized isomerization even though biacetyl phosphorescence was quenched at a rate nearly diffusion controlled ( $k_q = 7 \times 10^8 M^{-1} \text{sec}^{-1}$ ). In contrast, isomerization of **4** to **5** is sensitized by biacetyl. To check the possibility that lack of sensitization of the **1** → **3** conversion could be due to a quenching process not giving energy transfer,<sup>12</sup> fluorescence and isomerization of **1** were investigated in the presence of bromobenzene and iodobenzene, compounds which might be expected to induce intersystem crossing.<sup>14,15</sup> Bromobenzene did not quench fluores-

cence from **1** ( $\phi_f = 0.02$ ) at concentrations up to 1 *M*; however, iodobenzene proved to be an efficient quencher of fluorescence ( $K_{sv} = 0.64$ ) and concurrent with quenching of the fluorescence was an enhancement of  $\phi_{1 \rightarrow 3}$ .<sup>16</sup>

The above results suggest that triplets of **1** can serve as isomerization precursors<sup>18</sup> but do not preclude singlets as intermediates in the unperturbed direct isomerization. The observation that isomerization efficiencies from dienes **1**–**5** are relatively low suggests there is some inefficiency in each case in reaching the isomerization precursor and that radiationless decay of excited singlets having nearly the same geometry as the starting isomer is an important process. If we accept an allyl methylene as a reasonable model for the isomerization precursor,<sup>1,3</sup> the selective **1** ⇌ **3** interconversion indicates that this process involves exclusive decay from species **6**, even though **7** would be expected



to be as readily formed. The lack of a wavelength effect on the quantum yields apparently rules out selective population of a particular intermediate in the excitation process. The observation that irradiation of **2** leads to **3** and **1** further suggests that *formation* of an allyl methylene is not the product determining step since initial twisting in **2** would produce **7** or another allyl methylene but not **6**. The most consistent explanation appears to be that initial population of nearly planar excited states is followed by irreversible decay to equilibrating twisted allyl methylenes. All radiationless decay from the twisted states then proceeds from allyl methylene **6** to yield **1** and **3** as the photoisomerization products and the remarkable selectivity is thus accounted for in terms of selectively rapid decay processes from **6**. Interestingly considerations of intermediate stability suggest that **6** may not be the more stable allyl methylene or that there is at most relatively little difference in energy between **6** and **7**.<sup>19</sup> Except for the unusual selectivity observed here, the results are consistent with the model developed for equilibrating excited triplets of 2,4-hexadiene<sup>1,3</sup> where

(15) A. R. Horrocks, T. Medinger, and F. Wilkinson, *Chem. Commun.*, 452 (1965).

(16) Agreement between the Stern–Volmer constants for the two processes was satisfactory and **3** was the only product observed upon photolysis with iodobenzene. That isomerization does not come from a catalytic process is indicated by the finding that equilibration<sup>17</sup> of **1**, **2**, and **3** gives >99% **1** in each case.

(17) G. Fischer, K. A. Muszkat, and E. Fischer, *J. Chem. Soc. B*, 156 (1968).

(18) It is possible that iodobenzene quenches fluorescence by a process not involving triplet formation and that the sensitization experiments in fact involve formation of triplets of **1** that are inert to isomerization. The enhanced isomerization **1** → **3** in the presence of iodobenzene could then be due perhaps to decay of a diene–iodobenzene complex with isomerization or to quenching of **6** by iodobenzene with preferential decay to **3**.

(19) If a reasonable assumption that stabilization of the “methylene” portion of the allyl-methylene intermediate is most important is made, a comparison could be made based on stabilities of the radicals derived from 4-picoline and toluene. Although rates of H abstraction are more rapid for the latter compound, bond dissociation energies are estimated to be the same (77.5 kcal/mol).<sup>20</sup>

(20) K. M. Johnson and G. H. Williams, *J. Chem. Soc.*, 1446 (1960); W. V. Sherman and G. H. Williams, *ibid.*, 1442 (1963).

(8) The reaction was followed by vpc. **2** and **3** could be separated satisfactorily on a 22 ft column of XE-60 at 200° such that as little as 2–3% of the other isomer could be detected. The material balance between **1** and **3** was checked by addition, following irradiation, of an internal standard.

(9) A. Sandoval and L. Zechmeister, *J. Amer. Chem. Soc.*, **69**, 553 (1947).

(10) J. H. Pinckard, B. Wille, and L. Zechmeister, *J. Amer. Chem. Soc.*, **70**, 1938 (1948).

(11)  $\phi_{2 \rightarrow 3}$  could not be reliably measured at very low conversion although formation of **3** was easy to detect.<sup>8</sup> Both **2** and **3** were unstable on isolation as is **5**<sup>10</sup> so it was necessary to store the *cis*–*trans* isomers in the cold as dilute solutions in benzene.

(12) We have recently observed such phenomena with benzophenone and metal complexes as “sensitizers” and electron-deficient olefins as acceptors.<sup>13</sup> Here energy transfer does not compete favorably with other quenching processes (including electron transfer) even though it is energetically favorable and should proceed at rates nearly diffusion controlled.

(13) A. R. Gutierrez, C. R. Bock, and D. G. Whitten, unpublished results.

(14) T. Medinger and F. Wilkinson, *Trans. Faraday Soc.*, **61**, 620 (1965); **62**, 1785 (1966).

a sufficiently long excited-state lifetime permits a chain mechanism<sup>3a</sup> to operate. We are currently examining isomerization behavior of other 1-4 aryl-substituted butadienes and trienes both to determine the extent of this selectivity and the mechanism of the rapid-selective deactivation.

**Acknowledgment.** We thank the U. S. Public Health Service (Grant No. GM 15,238) for support of this work.

(21) Alfred P. Sloan Foundation Fellow.

Leslie R. Eastman, Jr., Bizhan M. Zarnegar  
James M. Butler, David G. Whitten\*<sup>21</sup>

Department of Chemistry, University of North Carolina  
Chapel Hill, North Carolina 27514

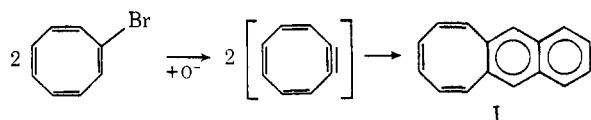
Received December 14, 1973

### The Cyclooctatrienyl Anion Radical

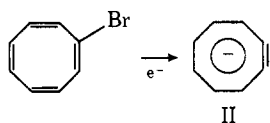
Sir:

Benzynes has stirred considerable chemical interest but has just very recently been observed under conditions conducive to general spectrometric observation.<sup>1</sup> Here we wish to report the preparation and observation of a new anion radical, which from all indications is the anion radical of cyclooctatrienyl (II). This anion radical is the eight-member nine-electron analog of benzyne.

Monobromocyclooctatetraene will react with strong base (potassium *tert*-butoxide) in etheral solvents to form naphthocyclooctatetraene.<sup>2</sup> This product is believed to be formed from the dimerization of cyclooctatrienyl as shown below.



We have attempted to trap the reactive cyclooctatrienyl as its anion radical. This was accomplished by allowing a solution of bromocyclooctatetraene to react in a mixture of 98% tetrahydrofuran and 2% HMPA<sup>3</sup> with a potassium mirror at  $-100^\circ$  under high vacuum. The esr pattern of this solution (Figure 1) consists of three triplets each due to two equivalent protons with coupling constants of 2.92, 3.55, and 4.06 G. There is also a splitting of 0.28 G due to the potassium cation. This esr pattern was observed at  $-100^\circ$  and disappears irreversibly at about  $-80^\circ$ .



This set of coupling constants is perfectly consistent with that expected for II. The coupling constant for the eight equivalent protons of cyclooctatetraene is 3.21 G,<sup>4</sup> and the average proton splitting for the new radical

(1) O. L. Chapman, K. Mattes, C. L. McIntosh, J. Pacansky, G. V. Calder, and G. Orr, *J. Amer. Chem. Soc.*, **95**, 6134 (1973).

(2) A. Krebs, *Angew. Chem.*, **77**, 966 (1965).

(3) HMPA (hexamethylphosphoramide) was purified as previously described: G. R. Stevenson, L. Echegoyen, and L. R. Lizardi, *J. Phys. Chem.*, **76**, 1439 (1972).

(4) H. L. Strauss, T. J. Katz, and G. K. Fraenkel, *J. Amer. Chem. Soc.*, **85**, 2360 (1963).

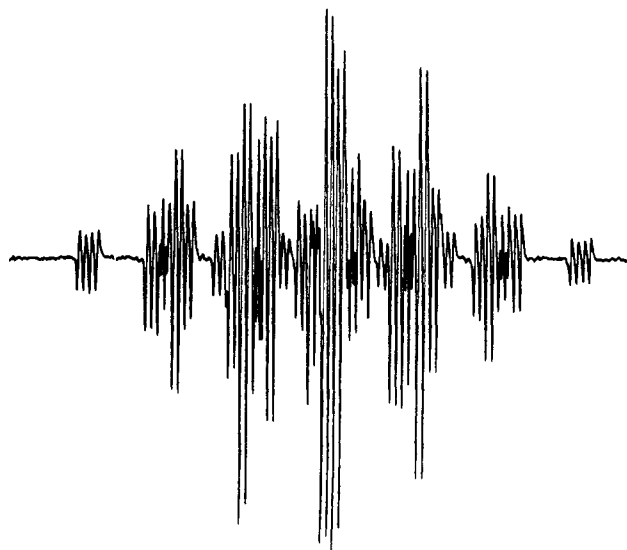


Figure 1. Esr spectrum of II at  $-100^\circ$  in tetrahydrofuran with added HMPA.

is 3.5 G. The fact that this average splitting is close to that for cyclooctatetraene indicates that the new radical is a perturbed cyclooctatetraene type anion with two protons missing.

The possibility existed that the new radical was simply the anion radical of the known cyclooctatetraene dimer (I). However, the reduction of I under the same conditions gave a radical yielding an entirely different esr spectrum consisting of more than 100 hyperfine lines.

It is also conceivable that the esr pattern for the new radical was due to the monobromocyclooctatetraene anion radical or the anion radical of some other monosubstituted cyclooctatetraene. This possibility was ruled out by the fact that all other monosubstituted cyclooctatetraene anion radicals, including those of *tert*-butoxycyclooctatetraene, ethylcyclooctatetraene, and phenylcyclooctatetraene, exhibit a pentet of quartets for the ring protons.<sup>5</sup> The esr coupling constants for the three sets of triplets observed for II are assigned and compared to those obtained from an INDO open shell calculation in Table I.

Table I. Calculated and Experimental Coupling Constants

Position	$a_H(\text{exptl})$ , G	$a_H(\text{calcd})^a$ , G	$a_H(\text{calcd})^b$ , G
1, 2			
3, 8	4.06	4.87	4.71
4, 7	2.92	0.78	1.38
5, 6	3.55	3.26	3.06

<sup>a</sup> The following bond distances were used for this INDO calculation: the C-C triple bond is 1.258 Å, all other C-C bonds are 1.415 Å, and C-H bonds are 1.08 Å. <sup>b</sup> This calculation was carried out using the same bond distances except that the C-C triple bond was considered to be 1.355 Å.

(5) (a) G. R. Stevenson and J. G. Concepcion, *J. Phys. Chem.*, **78**, 90 (1974). (b) The reduction of (phenyl-*ds*)cyclooctatetraene results in an anion radical that yields a pentet of 3.68 G due to four equivalent protons and a quartet of 2.38 G due to three equivalent protons in HMPA.