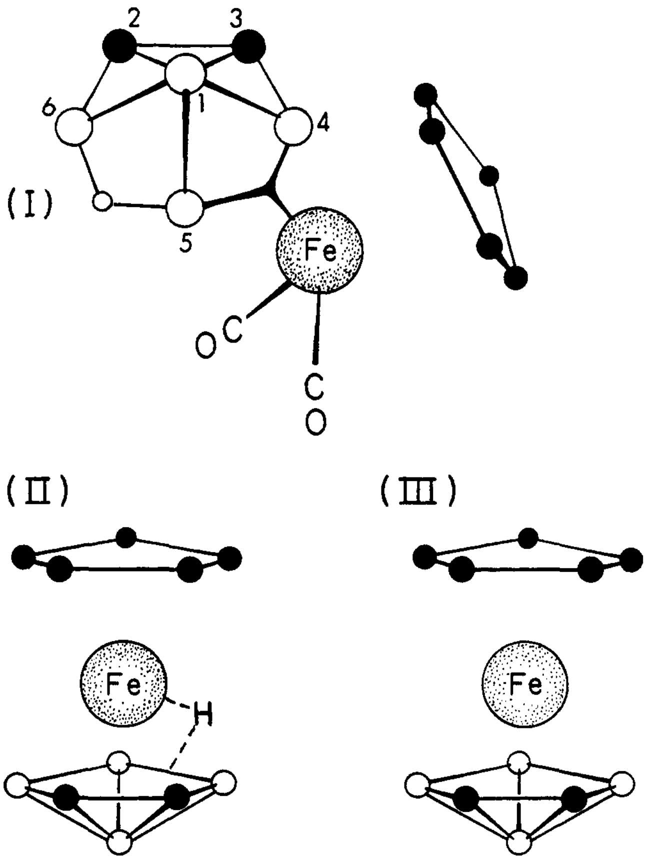

Figure 1. Proposed structures of μ-[(π-C_5H_5)Fe(CO)$_2$]$C_2B_4H_7$ (I), (π-C_5H_5)Fe^{II}(π-$C_2B_4H_7$) (II), and (π-C_5H_5)Fe^{III}(π-$C_2B_4H_6$) (III). The solid circles represent CH groups and the open circles BH groups. A possible location for the anomalous hydrogen atom in II, involving partial bonding to iron and to the carborane cage, is indicated schematically. If an Fe–H bonding interaction exists in II, the C_5H_5 and carborane rings are likely to be skewed relative to each other.

which we suggest schematically in Figure 1 (II), is that of a hydrogen which is partially bonded both to the iron atom and to the carborane cage.

The expected paramagnetism of III is confirmed by the broad, widely separated ^{11}B and ^{1}H nmr resonances and by the paramagnetic resonance spectrum (to be described in a subsequent paper). The only peaks observed in the ^{11}B nmr spectrum are humps at δ +154 and +281 with half-widths of $\sim$375 and 900 Hz, respectively. For comparison, the ^{11}B nmr spectra of paramagnetic iron(III) dicarbollyl complexes (*e.g.*, (π-C_5H_5)Fe(π-$C_2B_9H_{11}$)) exhibit broad singlets over a range of several hundred parts per million.[11] However, unlike the spectrum of III, those of the dicarbollyls are sufficiently well resolved to permit some correlation with structure.[11] We attribute the contrast to the presumably lesser average effect of the paramagnetic metal atom on the boron atoms of the large C_2B_9 cage, as compared to the effect on the C_2B_4 ligand in III, in which three of the four borons are directly bonded to iron.

The proton nmr spectrum of III contains a peak at δ −12.35 ($W_{1/2}$ = 300 Hz, area 5) assigned to the cyclopentadienyl ring, a resonance of area 2 at +7.35 ($W_{1/2}$ = 235 Hz) attributed to the carboranyl C–H groups, and broad, largely overlapped humps at −3.35, −5.5, and +10.6 which are presumably H–(B) resonances appearing as singlets in the absence of BH coupling.[11]

The structures, chemistry, and spectroscopic properties of these new complexes are under further investigation and will be presented in detail at a later date.

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[11] M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, Jr., and P. A. Wegner, *J. Amer. Chem. Soc.*, **90**, 879 (1968).

Medium Effects on the Lifetime and Reactivity of Triplet Exciplexes

Sir:

Phenomena involving formation and reaction of exciplexes have been the subject of much recent investigation and some controversy.[1–11] It is generally agreed that transfer of charge contributes to the binding energy of a wide variety of exciplexes,[1–3,6–8] but whether charge transfer is generally the driving force behind exciplex formation or if other factors such as excitation–resonance are also important is a major area of controversy.[3–7] The same confusion exists to some degree as to whether an exciplex is best described as a delocalized excited species or as more nearly an activated ion pair. There has also been disagreement as to whether exciplexes decay to ions in polar solvents or whether observed ions are formed directly *via* different processes.[8–12] While useful information regarding exciplex structure has been obtained from studies of exciplex emission and chemical reactions proceeding *via* exciplexes,[1,2,4,13–16] the short lifetimes of most exciplexes have necessitated a reliance on quenching data for solvent and structure–reactivity correlations.[5–9]

Recently we found that exciplexes formed by reaction of excited metalloporphyrin triplets and nitroaromatics have sufficient half-lives for observation by flash spectroscopy.[17] This direct observation technique has now been extended to investigate several

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[1] B. Stevens, *Advan. Photochem.*, **8**, 161 (1971).
[2] A. Weller, *Pure Appl. Chem.*, **16**, 115 (1968).
[3] D. Rehm and A. Weller, *Isr. J. Chem.*, **8**, 259 (1970).
[4] M. T. McCall, G. S. Hammond, O. Yonemitsu, and B. Witkop, *J. Amer. Chem. Soc.*, **92**, 6991 (1970).
[5] D. A. Labianca, G. N. Taylor, and G. S. Hammond, *ibid.*, **94**, 3679 (1972); G. N. Taylor and G. S. Hammond, *ibid.*, **94**, 3684, 3687 (1972).
[6] T. R. Evans, *ibid.*, **93**, 2081 (1971).
[7] J. B. Guttenplan and S. G. Cohen, *ibid.*, **94**, 4040 (1972).
[8] H. Leonhardt and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **67**, 791 (1968).
[9] D. Rehm and A. Weller, *ibid.*, **73**, 834 (1969); H. Knibbe, D. Rehm, and A. Weller, *ibid.*, **73**, 839 (1969).
[10] N. Mataga, T. Okada, and N. Yamamoto, *Chem. Phys. Lett.*, **1**, 119 (1967).
[11] T. Okada, H. Matsui, H. Oohora, H. Matsumoto, and N. Mataga, *J. Chem. Phys.*, **49**, 4717 (1968).
[12] Y. Taniguchi and N. Mataga, *Chem. Phys. Lett.*, **13**, 596 (1972).
[13] G. N. Taylor, *ibid.*, **10**, 355 (1971).
[14] E. A. Chandross and H. T. Thomas, *ibid.*, **9**, 393 (1971).
[15] E. A. Chandross and H. T. Thomas, *ibid.*, **9**, 397 (1971).
[16] I. G. Lopp, R. W. Hendren, P. D. Wildes, and D. G. Whitten, *J. Amer. Chem. Soc.*, **92**, 6440 (1970).
[17] J. K. Roy and D. G. Whitten, *ibid.*, **93**, 7093 (1971).

other triplet exciplexes formed with a variety of quenchers and excited states. In the present paper we report a study of medium effects on exciplex reactivity and decay. The results of this study suggest that exciplex phenomena may involve at least three intermediates—delocalized excited species, ion pairs, and free ions—depending upon the medium and the partners involved.

The exciplexes formed between triplet metalloporphyrins and electron-deficient aromatic compounds in hydrocarbon solutions are evidently true delocalized excited species. We find that they are quenched by oxygen and by several substances having low-lying triplets such as azulene (E_T = 31 kcal/mol) and tetracene (E_T = 29 kcal/mol) at rates near diffusion controlled. Table I lists data for a representative system, zinc etioporphyrin I–*p*-nitrotoluene (**1**) in benzene. That energy transfer occurs is indicated, since quenching of **1** with tetracene results in formation of the tetracene triplet.

Table I. Quenching of Excited States and Triplet Exciplexes[a]

Excited donor	Quencher	k_q, M^{-1} sec^{-1} Benzene	 Benzene–*N*-methylformamide[b]	 *N*-Methylformamide
1[c]	Azulene	2.6×10^9		No quenching[d]
1	Tetracene	5.1×10^8		No quenching
1	Perylene	1.3×10^9		
Zinc etioporphyrin I	PNT	3×10^9	2×10^8	1.3×10^8

[a] Degassed solutions, k_q values determined by flash spectroscopy. [b] 0.01 *M* NMF in benzene. [c] **1** is generated from 5×10^{-5} *M* zinc etioporphyrin I and 0.01 *M* PNT. [d] Transient half-life not reduced.

We[17] and others[9–12] have observed that exciplexes frequently show decreased lifetimes with increase in medium polarity. For **1** the half-life decreases from 92 to 32 μsec on addition of 0.01 *M* *N*-methylformamide (NMF). Having observed a decrease in exciplex half-life on addition of small amounts of NMF to benzene solutions, we were somewhat surprised to find a sharp *increase* in half-life when the NMF concentration was increased beyond 0.02 *M*. Careful investigation of **1** (as well as several other donor–quencher combinations) revealed that similar patterns are followed for a variety of polar substances; addition of the more polar component to benzene solutions first causes a decrease in transient half-life and subsequently a rapid increase to a limiting value (Figure 1). For **1** increases in medium polarity are accompanied by changes in both transient spectra and transient decay characteristics. The transient generated in benzene has intense absorption in the region 420–480 nm and little absorption above 600 nm; the transients generated in more polar media absorb strongly near both 450 and 650 nm. The latter spectra resemble those of π-cation radicals generated by one-electron oxidation of zinc and magnesium porphyrins.[18,19] Concurrent to the increase in transient half-life for **1** with addition of polar substances is a change in decay kinetics from first to second order (Figure 1). In contrast to the situation with the transients generated in benzene, decay of the latter species is not affected by addition of oxygen, azulene, or tetracene. Transients having nearly identical half-lives and spectra are generated from **1** and from zinc etioporphyrin I–*p*-benzoquinone in ethanol, where it has previously been shown by esr that electron transfer to yield ions is the dominant reaction.[16,20,21] The preceding evidence suggests that the long-lived transients in more polar media are the metalloporphyrin π cation and a negative ion derived from *p*-nitrotoluene (PNT). The half-life of these ions should be limited by diffusion-controlled recombination; a half-life of ~200 μsec is predicted from an estimation that $[\text{ions}]_0 = 10^{-6}$ *M* and $k_{\text{diff}} = 5 \times 10^9$ M^{-1} sec^{-1}. This is in reasonable agreement with the values of 180–300 μsec obtained for a variety of different systems using triplet zinc etioporphyrin I as the excited donor.

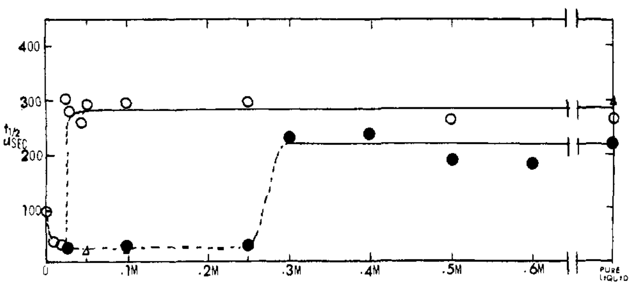

Figure 1. Transient half-life for **1** as a function of added polar cosolvent to benzene solutions. Added solvent: (○) *N*-methylformamide, (●) ethanol, (△) acetonitrile. (——) region where second-order decay is observed; (-----) region of first-order decay.

We interpret the present results to indicate that a transition in exciplex structure occurs from a relatively long-lived delocalized excited complex to an ion pair on increase in medium polarity.[10,11] The ion pair probably has a very short half-life due to inability of an individual ion to escape from the Coulomb field of its countercharge;[22] free ion formation in more polar media causes an increase in half-life along with a change to second-order decay. Since excited state quenching constants[23] (Table I) show only a small *decrease* on addition of polar substances and since only one type of transient is observed in each case, the present phenomena probably involve changes in exciplex structure and decay paths rather than additional excited state quenching processes.

An interesting result of the present study is the finding that addition of only small amounts (0.1–0.5 *M*) of polar components (ethanol, acetonitrile, or NMF) to benzene is required to convert the exciplex or ion pair with first-order decay to "free ions" having second-order decay. The changes occur at roughly the same solvent composition for a variety of donors (perylene, tetracene, and metalloporphyrins) and quenchers (*p*-benzoquinone, nitroaromatics, and *N*,*N*-dimethylaniline) under conditions where the mixture dielectric

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(18) J. H. Fuhrhop and D. Mauzerall, *J. Amer. Chem. Soc.*, **91**, 4174 (1969).

(19) Quenchers giving nearly identical spectra with zinc etioporphyrin I include PNT, methylacridinium fluoroborate, other nitroaromatics, and quinone.

(20) R. A. White and G. Tollin, *J. Amer. Chem. Soc.*, **89**, 1253 (1967); A. K. Bannerjee and G. Tollin, *Photochem. Photobiol.*, **5**, 315 (1966).

(21) B. J. Hales and J. R. Bolton, *J. Amer. Chem. Soc.*, **94**, 3314 (1972).

(22) R. C. Jarnagin, *Accounts Chem. Res.*, **4**, 420 (1971).

(23) Presumably these are exciplex formation constants; a discussion of the kinetics is deferred to a full paper.

constant is very close to that of benzene ($\kappa = 2.2$).[24] That solvent dielectric constant is not the controlling factor[22] is indicated by the finding that ions are not produced for any of these systems in tetrahydrofuran ($\kappa = 7.4$). Further study is planned to determine the influence of medium on the transition between excited complex, ion pair, and free ions in other systems.[25]

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[24] J. Timmermans, "The Physico-chemical Constants of Binary Systems in Concentrated Solutions," Vol. I and II, Interscience, New York, N. Y., 1959.

[25] Support of this work by the UNC Materials Research Center and the U. S. Public Health Service (Grant No. GM 15,238-05) is gratefully acknowledged.

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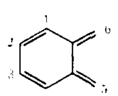
Stereospecific Synthesis of the (*E*,*E*)- and (*Z*,*E*)-5,6-Diphenyl-*o*-xylylene Dianions. Stereochemistry of Cycloreversion of the *cis*- and *trans*-3,4-Diphenylbenzocyclobutene Anion Radicals

Sir:

o-Xylylene (**1**) and its (*Z*,*E*)- and (*E*,*E*)-5,6-diphenyl derivatives **2** and **3** have been reliably inferred as transient intermediates near room temperature,[1,2] but no electronated species (*e.g.*, anion radicals or dianions) have been observed in this series. The present report describes a stereospecific synthesis of the dianions of **2** and **3** (2^{2-} and 3^{2-}). These are by far the most stable *o*-xylylene derivatives yet observed and, indeed, are the only ones known in which the *o*-xylylene structure is more thermodynamically stable than the contending benzocyclobutene one. The synthesis is additionally significant because it elucidates, for the first time, the preferred rotational stereochemistry of an electrocyclic reaction of an anion radical.



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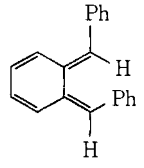

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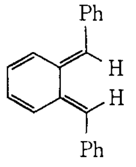

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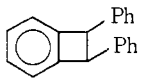

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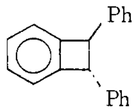

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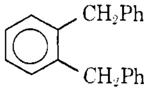

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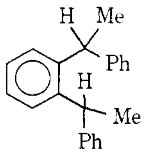

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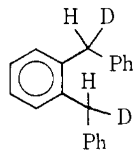

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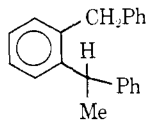

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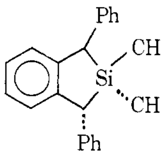

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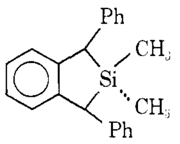

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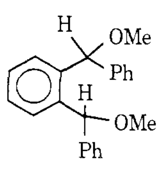

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cis- and *trans*-3,4-diphenylbenzocyclobutene (**4** and **5**, respectively) were prepared by the method of Carpino.[3] Birch reduction ($Na-NH_3-EtOH$) of each gave *o*-dibenzylbenzene (**6**) in quantitative yield, indicating facile cleavage of the 3,4 bond of the cyclobutane ring of the anion radicals of **4** and **5** ($4^{\cdot -}$ and $5^{\cdot -}$) even at −78°. Attempts to observe $4^{\cdot -}$ and $5^{\cdot -}$ (esr) by the usual alkali metal–ethereal solvent procedures were totally unsuccessful, thus confirming the instability of these anion radicals and, together with the Birch reduction results, suggesting that they cyclorevert rapidly to $2^{\cdot -}$ and/or $3^{\cdot -}$ which are rapidly converted to the diamagnetic dianions. Therefore, 2^{2-} and 3^{2-} were sought. The reactions of **4** and **5** with potassium in 2-methyltetrahydrofuran (MTHF) at −78° *in vacuo* were complete within 2 hr. That the resulting deep red solutions contained essentially only the desired dianions was indicated by quenching them with excess methyl iodide and with D_2O. The dimethyl and dideuterio compounds **7** and **8** were formed in >90% yield. The absence of monomethyl product **9** was further confirmed by independent synthesis. The two diastereoisomers of **7** were produced in *ca.* the same proportions from either **4** or **5** and have nmr ($CDCl_3$) τ 2.4–30 (14 H, m), 5.6 (2 H, q, $J = 7$ Hz), 8.4 (6 H, d, $J = 7$ Hz, 25% of this diastereoisomer), 8.6 (6 H, d, $J = 7$ Hz, 75%); mass spectrum *m/e* 286 (M).

The dianions from **4** and **5** can be confidently assigned the *Z*,*E* (2^{2-}) and *E*,*E* (3^{2-}) structures, respectively, on the basis of their reactions with dimethyldichlorosilane (−78°, MTHF, vacuum line). The dianion from **4** gave silanes **10** (84%) and **11** (16%) in >90% total yield, while that from **5** yielded **10** (30%) and **11** (70%), also in very high yield. Silane **10** has nmr (CS_2) τ 2.7–3.15 (14 H, m), 6.15 (2 H, s), 9.9 (6 H, s), mass spectrum *m/e* 314 (M), while **11** has nmr (CS_2) τ 2.6–3.1 (14 H, m), 6.35 (2 H, s), 9.6 (3 H, s), 10.4 (3 H, s); and mass spectrum *m/e* 314 (M). The methyl groups of the cis adduct **11** are nonequivalent whereas those of the trans adduct **10** are equivalent. Since any preference in the quenching reactions should be for suprafacial rather than antarafacial addition, the reaction sequences must be $4 \rightarrow 4^{\cdot -} \rightarrow 2^{\cdot -} \rightarrow 2^{2-} \rightarrow 10$ and $5 \rightarrow 5^{\cdot -} \rightarrow 3^{\cdot -} \rightarrow 3^{2-} \rightarrow 11$. Both cycloreversions (of $4^{\cdot -}$ and $5^{\cdot -}$) are therefore at least predominantly conrotatory. Note that the reactions of 2^{2-} and 3^{2-} with the silane are probably stepwise and thus not completely stereospecific.

Further confirmation of the dianion structural assignments and evidence that both cycloreversions are highly stereospecific are provided by nmr studies of the dianions in THF-d_8 (vacuum line preparation, sealed tube studies at −78° to room temperature). Dianion 2^{2-} has nmr τ 2.8 (4 H, m, meta), 3.5 (6 H, m, para, ortho), 4.1 (4 H, m, $H_{1,2,3,4}$), 5.77 (1 H, s, H_5 (outside benzylic proton)), 6.28 (incompletely resolved from solvent peak, s, H_6); 3^{2-} has nmr τ 2.7 (4 H, m, meta), 3.4 (6 H, m, ortho, para), 3.93 (2 H, m, $H_{2,3}$), 4.40 (2 H, m, $H_{1,4}$), 5.77 (2 H, s, $H_{5,6}$). The positional assignments, except for the benzylic protons, are based in part

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[1] N. L. Bauld, C.-S. Chang, and F. R. Farr, Jr., *Tetrahedron Lett.*, 2443 (1972).

[2] R. Huisgen and H. Seidl, *ibid.*, 3381 (1964).

[3] L. A. Carpino, *J. Amer. Chem. Soc.*, **84**, 2196 (1962).