species other than metal ions, provided that a labile complex is formed and that scalar coupling is effectively negligible. Thus, the possibility of determining molecular conformation with respect to spin labels and rare earth shift reagents is indicated.[16] The method is thus complementary to that of conformational determination from rare earth shift measurements.[17] Applications to large molecular complexes are limited only by the ability to resolve and assign proton resonance lines.

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(16) This application of lanthanide shift reagents has been proposed independently by H. N. Cheng.

(17) W. D. Horrocks and J. P. Sipe, *J. Amer. Chem. Soc.*, **93**, 6800 (1971).

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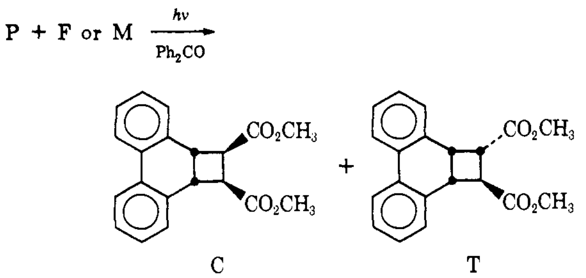
Intermediates and Stereochemistry in the Triplet-State Photocycloaddition of Phenanthrene to Electron-Poor Olefins

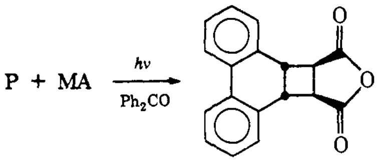
Sir:

The intermediacy of singlet excited-state complexes (exciplexes) in singlet-state [2 + 2] photocycloadditions is well documented;[1] it is common, if not universal. By contrast, triplet exciplexes in sensitized photocycloadditions stand on less firm ground. Evidence in their support has been largely inferential.[2] The extreme difficulty of observing exciplex phosphorescence,[3] and the expectation that triplet exciplexes will show substantially less binding energy than singlet exciplexes,[4] make their importance a moot point. Our recent[5] indirect demonstration of a triplet exciplex in the Paterno–Buchi reaction of diaryl ketones led us to examine other systems. A recent report[6] of the reaction of phenanthrene (P) with dimethyl fumarate (F) prompts us to report the results of our own study of this and related reactions. We have observed patterns of reactivity and stereoselectivity that suggest a triplet exciplex intermediate.

The benzophenone-photosensitized cycloaddition of phenanthrene to F, dimethyl maleate (M), and maleic anhydride (MA) leads to the photocycloadducts C, T, and CA of eq 1 and 2. The structures of these adducts follow from their satisfactory analyses, their nmr spectra, the conversion of C to T with sodium methoxide in dry methanol, the conversion of CA to C with acidic methanol, and the ozonolysis of C (acetic acid solvent, hydrogen peroxide work-up, and diazomethane esterification) to the known[7] *cis,trans,cis*-cyclobutane-1,2,3,4-tetracarboxylic acid tetramethyl ester. In the reaction with MA,[8] less than 5% of an endo anhydride isomer was formed as evidenced by the nmr of reaction mixtures. In the reaction with F or M, the unknown cis,endo isomer was absent (<3%), as evidenced by the nmr spectra and glpc analysis of reaction mixtures; ozonolysis of reaction mixtures revealed none (<2%) of the all-cis cyclobutane tetraester.[7] Material balance (±3%) was maintained throughout, by comparison of P + C + T with P(initial) and F + M + C + T with M or F(initial). This was true even in prolonged irradiation (eight times the time necessary for 90% conversion).

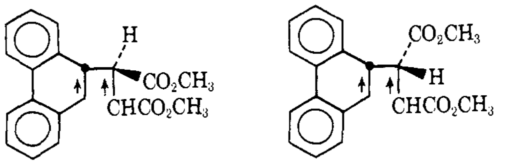


C T (1)



CA (2)

The ratio of T to C was 1.8 ± 0.05, independent of reaction time and of whether F or M was the reactant.[9] Although concomitant F to M and M to F isomerization occurred, we were able to observe this same T:C ratio in experiments in which isomerization of F to M was as low as 0.9% or M to F as low as 1.2%. The intermediacy of a triplet 1,4-biradical intermediate, analogous to those proposed in other triplet-state photocycloadditions,[1b,2,5,10] is thus indicated. Quantum yield studies confirmed that P^3 and not F^3 is the reactive species and that its probability of ultimate conversion to C + T is 0.11 (Figure 1).



SR *SS*

Two stereoisomeric biradicals, *SR* and *SS*, are possible. Both C and T can be formed from *SR*, but *SS* would give the isomeric cis,endo diester in addition to T. If a biradical is precursor to CA, it must also have the *SR* stereochemistry. Our product ratios in-

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(1) (a) I. M. Hartmann, W. Hartmann, and G. O. Schenk, *Chem. Ber.*, **100**, 3146 (1967); (b) D. O. Cowan and R. L. E. Drisko, *J. Amer. Chem. Soc.*, **92**, 6281, 6286 (1970); (c) H. Morrison, H. Curtis, and T. McDowell, *ibid.*, **88**, 5415 (1966); (d) O. L. Chapman and R. D. Lura, *ibid.*, **92**, 6352 (1970); (e) N. J. Turro, P. A. Wriede, and J. C. Dalton, *ibid.*, **90**, 3274 (1968).

(2) (a) E. J. Corey, J. D. Bass, R. Le Mahieu, and R. B. Mitra, *ibid.*, **86**, 5570 (1964); (b) P. DeMayo, *Accounts Chem. Res.*, **4**, 41 (1971); (c) I. Kochevar and P. J. Wagner, *J. Amer. Chem. Soc.*, **92**, 5742 (1970); **94**, 3859 (1972); (d) C. DeBoer, *ibid.*, **91**, 1855 (1969).

(3) Th. Forster, *Angew. Chem., Int. Ed. Engl.*, **8**, 33 (1969), and references therein.

(4) A. K. Chandra and E. C. Lim, *J. Chem. Phys.*, **49**, 5066 (1968).

(5) (a) R. A. Caldwell and S. P. James, *J. Amer. Chem. Soc.*, **91**, 5184 (1969); (b) R. A. Caldwell, *ibid.*, **92**, 1439 (1970).

(6) S. Farid, J. C. Doty, and J. L. R. Williams, *J. Chem. Soc., Chem. Commun.*, 711 (1972).

(7) Dr. J. W. Young provided authentic samples for comparison; *cf.* J. Meinwald and J. W. Young, *J. Amer. Chem. Soc.*, **93**, 725 (1971).

(8) D. Bryce-Smith and B. Vickery, *Chem. Ind.* (London), 429 (1961).

(9) Prolonged irradiation causes T → C isomerization without significant material loss. Isolation of T or C is best accomplished by fractional crystallization from methanol of the product mixture derived from either short-term (for T) or long-term (for C) irradiation.

(10) (a) P. D. Bartlett, *Quart. Rev., Chem. Soc.*, **24**, 473 (1970); (b) D. R. Arnold, *Advan. Photochem.*, **6**, 301 (1968); (c) W. L. Dilling, T. E. Tabor, F. P. Boer, and P. P. North, *J. Amer. Chem. Soc.*, **92**, 1399 (1970).

dicate that M and F produce the same proportion of *SR* and *SS* (else the isomer which produced more *SS* would also have afforded a higher T:C ratio). Clearly the simplest rationalization is that *the SR stereochemistry is strongly dominant if not exclusive.* This statement rejects as less palatable the alternatives that M and F fortuitously afford the same finite ratio of biradicals or that *SS* whenever formed undergoes quantitative β scission. Preferential positioning of the substituent on the first-formed bond in an exo position, as in *SR*, *might* result from a steric effect; however, we note recent theoretical support[11] from calculations of the geometry of the benzene-maleic anhydride system[12] for an *electronic* contribution directing exo product if an exciplex intervenes.

Table I. Rate Constants for Quenching of Phenanthrene (P) Excited States by Dimethyl Fumarate (F) or Dimethyl Maleate (M)

Reactant	E_T,[a] kcal/mol	Quencher	k,[b] M^{-1} sec^{-1}
P (singlet)		M	$8 \pm 1 \times 10^8$ [d]
P (singlet)		F	$7.5 \pm 1 \times 10^9$ [e]
P (triplet)	62.0	M	$4 \pm 2 \times 10^7$ [f]
P (triplet)	62.0	F	1.35×10^9 [f]
3,6-Dimethoxy P (triplet)	62.7	F	1.9×10^9 [f]
2-Acetyl P (triplet)	62.1	F	7×10^8
1-Methyl-7-isopropyl P (triplet)	61.0	F	$8 \pm 1 \times 10^8$ [f]
9,10-Dimethyl P (triplet)	59.8	F	$2 \pm 0.5 \times 10^8$ [f]
3-Acetyl P (triplet)	59.4	F	4×10^7
9-Cyano P (triplet)	58.0	F	$<3 \times 10^7$ [c,f]

[a] Determined by Mr. Donald Friedrich at 77°K in 3-methylpentane. Precision ±0.1 kcal/mol. [b] Precision ±5% unless otherwise noted. [c] No quenching observed. [d] S. Farid (private communication) has found a comparable value. [e] S. Farid, *J. Chem. Soc., Chem. Commun.*, 711 (1972) has found 1×10^{10} M^{-1} sec^{-1}. [f] Benzophenone, or in some cases thioxanthone, sensitization at 3660 Å was used to obviate phenanthrene singlet quenching. A subsequent straightforward correction for energy transfer from sensitizer to F or stilbene was applied.

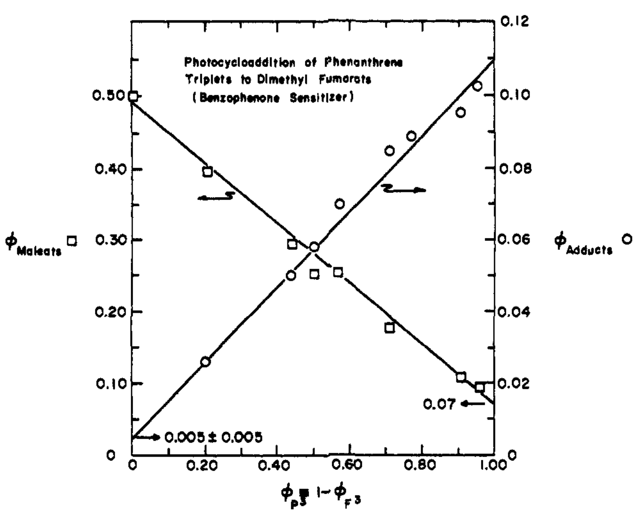

Figure 1. Quantum yields at 3660 Å of dimethyl maleate formation (left ordinate) and total cyclobutane adduct formation (right ordinate) from benzophenone sensitization of mixtures of phenanthrene and dimethyl fumarate. Here $\phi(P^3)$ is the yield of triplet phenanthrene in the mixture as calculated from P and F concentrations and independently determined rate constants of excitation transfer from benzophenone to P and F.

Table I presents kinetic data for M and F as quenchers of either phenanthrene fluorescence (τ = 60 nsec[13]) or of the phenanthrene- or substituted phenanthrene-sensitized isomerization of *trans*-stilbene ($k = 5 \times 10^9$ M^{-1} sec^{-1} assumed for the rate constant for excitation transfer to stilbene from all sensitizers). The following conclusions arise. (1) The triplet quenching rate constants, while slightly lower than those for phenanthrene singlet, are very large and in particular are far larger than would be expected for a simple radical-like addition of P^3 to F. (2) For both P^1 and P^3, F is a considerably better quencher than M. (3) Triplet quenching rate constants generally increase with increasing triplet energy of the phenanthrene.

The possibility that the triplet rate constants are dominated by excitation transfer, leading to a trivial explanation of point (3), seems remote in view of the inefficiency with which phenanthrene triplet sensitized isomerization of F to M occurs (ϕ = 0.07; Figure 1) relative to benzophenone triplet sensitized isomerization (ϕ = 0.50; Figure 1). Since the latter value sets a lower limit for the decay fraction of $F^3 \rightarrow M$, the upper limit for the yield of F^3 from the interaction of P^3 and F is 14%.

We believe the kinetic data are sufficient to postulate a triplet exciplex intermediate in this reaction, presumably identical with the one obtained from direct irradiation *via* intersystem crossing in the singlet exciplex.[6] Unexpectedly large rate constants observed in the Paterno–Buchi reaction were also associated with excited-state complex formation.[2c,5] The triplet excitation energy of F (61–67 kcal/mol[14]) is a better match than that of M (72–77 kcal/mol[14]) for P^3, a condition contributing to maximization of exciplex stabilization and presumably also of rate of exciplex formation. The increase of rate with E_T of the phenanthrene is expected on the same basis; however, the rough parallel of E_T with the electron-donating power of the substituent leaves it also possible that the most important contributor to the exciplex binding is electron transfer from phenanthrene to olefin. In support of electron transfer binding, we note that β-methylstyrene (E_T = 59.8,[15] trans; *ca.* 70, cis[16]), an olefin of similar triplet energy but without strong electron-attracting groups, in our hands affords no detectable cycloaddition product with phenanthrene triplet.

In summary, we believe that the mechanism[2a,5b] for triplet state [2 + 2] photocycloaddition involving a triplet exciplex as precursor of a 1,4 biradical has considerable generality. Studies of binding mechanisms, geometries, and energies will be rewarding.

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(12) D. Bryce-Smith, B. Vickery, and G. I. Fray, *J. Chem. Soc. C*, 390 (1967).

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(14) G. S. Hammond, *et al.*, *J. Amer. Chem. Soc.*, **86**, 3197 (1964).

(15) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

(16) G. W. Sovocool, Ph.D. Thesis, Cornell University, 1971.

forming the ozonolyses. Ms. Mary McKenney Ulrich performed valuable preliminary experiments.

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Chemically Induced Dynamic Nuclear Polarization Detection of Selective Iron-Catalyzed Radical Formation from an Alkyl Halide in the Presence of Its Grignard Reagent

Sir:

It has long been recognized that the reaction between Grignard reagents and alkyl halides is catalyzed by the addition of salts of transition metals (the Kharasch reactions).[1] The role played by the catalytic species is, however, unknown. Kochi[2] has recently found the rate of the iron salt catalyzed reaction to be first order in the concentrations of halide and catalyst but independent of Grignard concentration. The evidence from deuterium labeling, which we present here, supports separate reaction pathways for the halide and Grignard reagent. Furthermore, we provide CIDNP data which allow us to draw mechanistic conclusions about these systems which are virtually unobtainable by product analysis alone.

The rapid ($t_{1/2} \simeq 3$ min) reaction of a tetrahydrofuran solution 0.7 *M* in 2-propylmagnesium bromide, 1.4 *M* in 2-deuterio-2-propyl bromide, and 7×10^{-6} *M* in either ferrous or ferric chloride[3] (reaction 1a) produces propene-d_0 and -d_1 in a ratio of approximately 3:2, propane-d_0 and -d_1, and smaller amounts of 2,3-dimethylbutane (Scheme I). In the absence of metal catalysts, less than 5% reaction occurs in 1 hr. Reversing the label (reaction 1b) produces the same products, although the deuteriopropene is now the favored alkene.

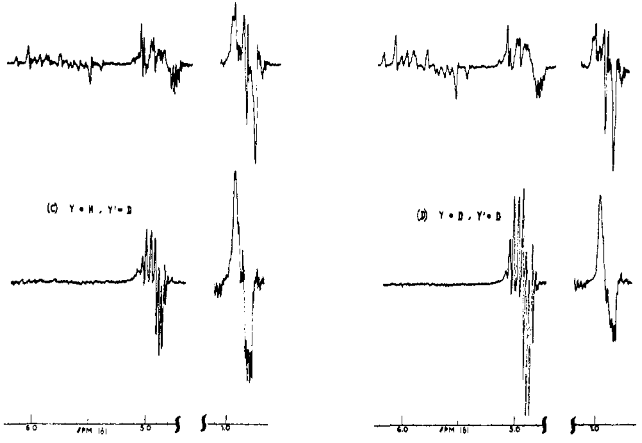

Figure 1. CIDNP spectra recorded during the ferrous chloride catalyzed reaction of $(CH_3)_2CYMgBr$ with $(CH_3)_2CY'Br$ in tetrahydrofuran. For Y = H and Y′ = H (A) and Y = D and Y′ = H (B), the multiplet at δ 0.9 is propane and the multiplets at δ 4.9 and 5.7 are the methylene and methyne protons of propene, respectively. For Y = H and Y′ = D (C) and Y = D and Y′ = D (D), the multiplet at δ 0.9 is 2-deuteriopropane and the multiplet at δ 4.9 is the methylene protons of 2-deuteriopropene.

Scheme I

$$(CH_3)_2CHMgBr + (CH_3)_2CDBr \xrightarrow{FeCl_2}$$
$$\underset{43\%}{CH_3CD{=}CH_2} + \underset{57\%}{CH_3CH{=}CH_2} +$$
$$\text{propane (H + D) + coupling product} \quad (1a)$$

$$(CH_3)_2CDMgBr + (CH_3)_2CHBr \xrightarrow{FeCl_2}$$
$$\underset{61\%}{CH_3CD{=}CH_2} + \underset{39\%}{CH_3CH{=}CH_2} +$$
$$\text{propane (H + D) + coupling product} \quad (1b)$$

When the above reactions were carried out in the probe of an A-60-A nmr spectrometer, large polarizations (AE) for the hydrocarbon products were observed. In reaction 1a, only 2-deuteriopropene and 2-deuteriopropane are polarized (Figure 1C), while in reaction 1b only undeuterated propane and propane are polarized (Figure 1B).[4]

Figures 1A and 1D display the polarization resulting from the reactions of undeuterated Grignard with undeuterated halide and deuterated Grignard with deuterated halide, respectively.

The polarization displayed in Figure 1B resembles closely that in Figure 1A, and likewise, Figure 1C resembles Figure 1D. No alkyl exchange between the Grignard reagent and labeled alkyl bromide was detectable by nmr, in either the presence or absence of catalyst.

Three conclusions about the mechanism of the Kharasch reaction can be drawn from these observations. (1) The observation that unequal amounts of propene and deuterated propene are formed in these reactions indicates that a mechanism which involves disproportionation of an equal number of alkyl radicals derived from the organometallic reagent and the alkyl halide is not operative.[5] (2) The phase of the observed pure multiplet effect polarized (AE) indicates[6] that the hydrocarbon products are polarized during diffusive encounters of free radicals and is consistent with a free radical chain mechanism in which most radicals are not formed in pairs. (3) Free radicals are produced only from the alkyl halide since CIDNP is observed only in the products derived from the alkyl halide, although propane and propene are formed from both reactants.[7]

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[1] M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Non-Metallic Substances," Prentice-Hall, New York, N. Y., 1954, p 122 ff.

[2] M. Tamura and J. Kochi, *J. Organometal. Chem.*, 31, 289 (1971).

[3] Metallic impurities in the magnesium used to prepare the Grignard reagent apparently become catalytically active only if they are oxidized. This produces some interesting effects on the coupling reaction brought about by impurities in both the Grignard and alkyl halide; R. Allen, to be published.

[4] The polarized coupling product was difficult to observe due to the overlapping polarizations resulting from the methyl protons of the coupling product and propane. In reaction 1b, however, the polarized (AE) methyne protons of 2,3-dimethylbutane could be observed.

[5] A mechanism involving formation of radicals indiscriminately from both a halide and organometallic compound does, however, explain CIDNP data from the reaction of alkyllithium compounds with alkyl halides: see R. A. Cooper, H. R. Ward, and R. G. Lawler in "Chemically Induced Magnetic Polarization," G. L. Closs and A. R. Lepley, Ed., Wiley, New York, N. Y., 1972.

[6] H. R. Ward, *Accounts Chem. Res.*, 5, 18 (1972); R. G. Lawler, *ibid.*, 5, 25 (1972).

[7] The polarized propene lines are at least 30 times more intense than the corresponding lines of propene derived from the Grignard reagent. If free radicals are formed from the Grignard reagent they must therefore be quite ineffective in producing CIDNP. A tidier explanation is that they are simply absent.