disappears upon addition of D_2O), 6.98 (d, 1, $J = 3$ Hz, C_6 methine), 4.38 (m, 1, C_7 vinyl), 4.15 (d, 1, $J = 10$ Hz, C_3 vinyl), and 3.35 (d, 1, $J = 10$ Hz, C_4 vinyl); uv max (MeOH) 242 (ϵ 4000) and sh 330 nm (ϵ 30).

In addition, the structures of these photoproducts were indicated by a series of intriguing thermal and photochemical interconversions. Thus, sealed tube thermolysis of **6** at 200° gave a high yield of **5**. Analogous behavior was previously observed[3] for compounds **2** and **3**. Furthermore, sealed tube thermolysis of **7** at 200° for 5 hr gave a 70% isolated yield of isomer **5**, and photolysis of **7** in benzene ($\lambda > 340$ nm) afforded an 80% yield of **6**. That **6** is nevertheless a primary photoproduct of Diels–Alder adduct **4** in benzene was demonstrated by a time-dependence study which showed the build-up of both **6** and **7** at comparable rates without an induction period for the formation of **6**. Remarkably, photolysis of **7** in *tert*-butyl alcohol gave a high yield of photoisomer **5**. These reactions are summarized in Scheme I.

In contrast to the results of photolysis of Diels–Alder adduct **4**, irradiation of either benzene or *tert*-butyl alcohol solutions of Diels–Alder adduct **8** afforded, after column chromatography on neutral alumina, a 30% yield of the tricyclic product **9**, mp 80–80.5°, which possesses the basic patchouli alcohol[7] and seychellene[8] ring system. The structure of this material followed from its spectral characteristics: ir (CCl_4) 5.79 μ (C=O); nmr ($CDCl_3$) τ 4.1–4.6 (m, 2, vinyl H), 7.2–7.7 (m, 7), 7.7–8.4 (m, 2), and 8.7 (d, 3, $J = 7$ Hz, CH_3); $n \rightarrow \pi^*$ uv max (MeOH) 291 nm (ϵ 56); prolonged base-catalyzed deuterium exchange afforded replacement of only two hydrogens as shown by nmr.

An attractive possibility for the photochemical conversion of Diels–Alder adduct **4** into products **5**, **6**, and **7** involves initial formation of the resonance-stabilized intermediate **10** *via* a virtually unprecedented[9] carbon–oxygen β-hydrogen transfer. Bonding of species **10** as indicated in Scheme I would then lead directly to photoproduct **7** and to the enol forms of compounds **5** and **6**. The intermediacy of these enol forms is supported by the finding that photolysis of Diels–Alder adduct **4** in *tert*-butyl alcohol-*O-d* led to photoisomer **5** with one deuterium atom substituted exclusively in the exo-4 position.[10] The same product was obtained by mild base-catalyzed deuterium exchange of proteo ketone **5**.[11]

The source of the remarkable product dependence on solvent in the photolysis of **4** is less clear-cut. Explanations invoking the intermediacy of photoproducts **6** and/or **7** in the conversion of **4** to **5** in *tert*-butyl alcohol were ruled out by appropriate control experiments. The possibility exists that in *tert*-butyl alcohol, a zwitterionic intermediate such as **11**, stabilized by hydrogen bonding and solvation of the positive charge at C_8, may be responsible for the preferential formation of photoproduct **5** *via* 3,8 bonding. The reaction in benzene on the other hand could then be interpreted as occurring (through either a zwitterionic or a diradical intermediate) by preferential bond formation at the inductively stabilized C_6 position to give photoisomers **6** and **7**. Similar arguments can be brought to bear on the photochemical conversion of **7** to **5** in *tert*-butyl alcohol which in all probability also occurs *via* species **11**. Further studies on this point are planned.[12]

As pointed out previously,[3] the thermal conversions of **3** to **2**, and in this study, of **6** to **5**, are likely to be nonconcerted.[13,14] On the other hand, the photochemical reaction of **7** giving **6** in benzene and the thermal **7** to **5** conversion are formal examples of allowed [1,3] and [3,3] suprafacial sigmatropic rearrangements, respectively.[13] Whether these concerted pathways are in fact followed is uncertain in view of the probable low activation energies required for the corresponding nonconcerted processes.[15]

Finally, the difference in photochemical reactivity between Diels–Alder adducts **4** and **8** should be discussed. Possibly this difference (β-hydrogen abstraction *vs.* γ-hydrogen abstraction) is due to the inaccessibility of the β-hydrogens for abstraction in the preferred conformation of Diels–Alder adduct **8** (*cf.* structure **12**). An alternative conformation which brings the β-hydrogen atoms and the carbonyl groups into proximity introduces a severe methyl–methyl bowsprit–flagpole-like interaction. In support of these ideas is the finding that the Diels–Alder adduct **13**[16] is completely inert under the conditions used for the photolysis of adducts **4** and **8**.

Further product, mechanistic, and photophysical studies with a variety of quinone–diene adducts are in progress.

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(7) G. Büchi, W. D. MacLeod, Jr., and J. Padilla O., *J. Amer. Chem. Soc.*, **86**, 4438 (1964).

(8) G. Wolff and G. Ourisson, *Tetrahedron*, **25**, 4903 (1969).

(9) See A. Padwa and W. Eisenhardt (*J. Amer. Chem. Soc.*, **93**, 1400 (1971)) for a possible example.

(10) The extent, position, and stereochemistry of the deuterium substitution were proved by nmr and mass spectrometry; details will be published in the full paper.

(11) For other examples of preferential exo exchange in bicyclo[2.2.1]-heptan-2-ones, see T. T. Tidwell, *J. Amer. Chem. Soc.*, **92**, 1448 (1970), and references cited therein.

(12) Explanations for these solvent effects based on n,π^* (benzene) – π,π^* (*tert*-butyl alcohol) reactivity differences cannot be ruled out at the present time although it is difficult to see how these differences can be interpreted in terms of mechanism. Furthermore, if Diels–Alder adducts **1** and **4** resemble *p*-benzoquinone in the relative positioning of their n,π^* and π,π^* excited states (n,π^* much lower in both the singlet and the triplet, *cf.* H. E. Zimmerman, R. W. Binkley, J. J. McCullough, and G. A. Zimmerman, *ibid.*, **89**, 6589 (1967), and references cited therein), it is unlikely that a change to polar solvents will cause a level reversal. Emission spectroscopic studies and sensitization-quenching experiments are in progress to resolve these points.

(13) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

(14) J. A. Berson, *Accounts Chem. Res.*, **1**, 152 (1968).

(15) A reaction analogous to the photochemical **7** → **6** conversion has recently been reported and shown to be nonconcerted, *i.e.*, nonstereospecific: R. L. Cargill, B. M. Gimarc, D. M. Pond, T. Y. King, A. B. Sears, and M. R. Willcott, *J. Amer. Chem. Soc.*, **92**, 3809 (1970).

(16) Y. Lepage, *Bull. Soc. Chim. Fr.*, 2019 (1963).

John R. Scheffer,* Kuldip S. Bhandari
Rudolf E. Gayler, Rommert H. Wiekenkamp
Department of Chemistry, University of British Columbia
Vancouver 8, Canada

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Trapping by Mercaptans of the Biradical Intermediates in Type II Photoelimination

Sir:

Although the massed evidence for the intermediacy of 1,4 biradicals in triplet-state type II photoelimination processes is compelling,[1] no successful attempt to trap such a biradical has yet been reported,[2] despite

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(1) P. J. Wagner, *Accounts Chem. Res.*, **4**, 168 (1971).

(2) A nitroso compound traps a radical species produced by irradia-

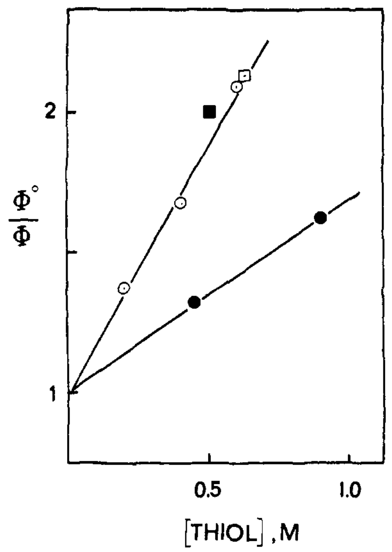


Figure 1. Quenching of type II reactions by thiols in benzene containing 1.2 M pyridine: ○, dodecyl mercaptan and γ-methoxybutyrophenone; □, dodecyl mercaptan and valerophenone; ●, butanethiol-S-d and γ-methoxybutyrophenone; ■, butanethiol and γ-methoxybutyrophenone with 2 M *tert*-butyl alcohol instead of pyridine.

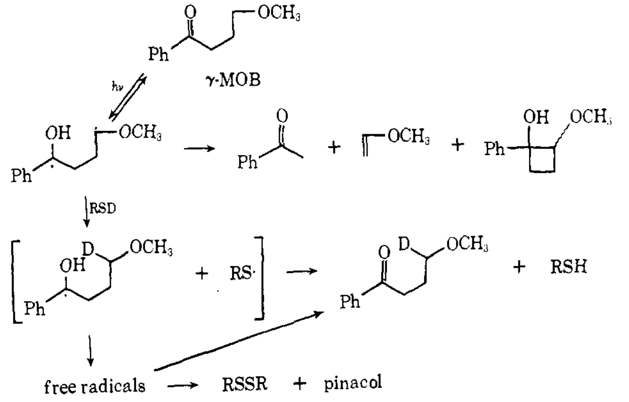
the fact that mere conjugated dienes apparently trap the 1,4 biradicals produced by photolysis of cyclobutanones.[3,4] We now find that alkyl mercaptans very efficiently trap the biradicals produced from phenyl alkyl ketones. The evidence comes from both kinetics and from labeling experiments.

Figure 1 displays a Stern–Volmer plot for the quenching of acetophenone formation from γ-methoxybutyrophenone (γ-MOB) by dodecyl mercaptan and by S-deuterated butyl mercaptan. The slopes indicate $k_q\tau_{BR}$ values of 1.8 and 0.7 M^{-1}. Evidence that the thiols are not trapping the excited triplet is provided by the following observations: (1) the reaction of valerophenone is quenched with equal efficiency, despite the fivefold difference in triplet lifetimes of the two ketones (τ 1.6 and 8 nsec);[1] (2) the efficiency with which n-butyl mercaptan quenches the phosphorescence of acetophenone in degassed benzene solutions[5] indicates a k_q value of 1.4 × 10^7 M^{-1} sec^{-1}, which rate constant predicts actual $k_q\tau_T$ values of only 0.11 and 0.023 M^{-1} for thiols toward triplet valerophenone and γ-MOB, respectively; (3) there is no deuterium isotope effect on phosphorescence quenching, but a threefold effect on type II quenching.

Irradiation (λ > 330 nm) of benzene solutions of γ-MOB containing large concentrations of butanethiol-S-d_1 results in extensive incorporation of deuterium specifically at the γ-carbon of unreacted, recovered γ-MOB. Mass spectral analysis (70 eV) reveals very similar values for the following m/e ratios, after correction for ^{13}C: (179 + 180)/178 (parent ion); 121/120 (MacLafferty acetophenone enol); most importantly, (46 + 47)/45 ($CH_3OCH_2^+$ cation resulting from cleavage of the β,γ C–C bond facilitated by the γ-methoxy group). Nmr analysis confirms the disappearance of γ protons both by the reduced relative intensity of the triplet centered at δ 3.2 and by the broadening of the original β-methylene quintet at δ 1.8 into an unresolved glob.

For a sample 0.2 M in γ-MOB and 2.7 M in C_4H_9SD, the following quantum yields were measured: ketone disappearance, 0.57; acetophenone formation, 0.27; cyclobutanol formation, 0.07; γ deuteration of γ-MOB, 0.33; dibutyl disulfide formation, 0.11. If the same quantum yield of 0.11 is assumed for formation of the pinacol from reduced γ-MOB (it crystallized out when the photosylate was concentrated, but we did not measure it quantitatively), we obtain a mass balance close to 100% for reacted ketone. This conclusion is in keeping with the clean nature of the reaction, absolutely no products other than those mentioned above being detected by vpc analysis. The total quantum yield of measurable reactions was 0.90, indicating that only 10% of the biradicals from γ-MOB returned to ground-state ketone.[7] Scheme I summarizes what seems to happen.

Scheme I



Unfortunately, values reported for rate constants of reactions of alkyl radicals with alkyl mercaptans range from 10^5 to 10^8 M^{-1} sec^{-1},[8–10] so that we cannot unequivocally assign τ_{BR} values from measured $k_q\tau_{BR}$ values. Since mercaptans and trialkylstannanes show similar efficiencies in intercepting monoradicals which undergo rapid intramolecular rearrangements,[11] and since stannanes are reported to trap alkyl radicals with rate constants ~10^6 M^{-1} sec^{-1},[12] we tentatively estimate τ_{BR} for the solvated biradical from valerophenone to be 10^{-6} sec.

Since we ran these thiol quenching experiments in the presence of enough added alcohol or pyridine to

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tion of neat butyrophenone or valerophenone, but the experiment was not performed so as to allow differentiation between a biradical or a monoradical produced by intermolecular hydrogen abstraction: K. Torssell, *Tetrahedron*, **26**, 2759 (1970).

(3) (a) P. Dowd, A. Gold, and K. Sachdev, *J. Amer. Chem. Soc.*, **92**, 5724 (1970); (b) N. J. Turro and D. M. McDaniel, *ibid.*, **92**, 5727 (1970).

(4) Typical rate constants for alkyl radical addition to conjugated dienes at 25° are ~10^6 sec^{-1}: W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966, pp 161, 223.

(5) Measured $k_q\tau_T$ values: 78 M^{-1} for C_4H_9SH; 73 M^{-1} for C_4H_9SD; 26,000 M^{-1} for 1,3-pentadiene, indicating a triplet τ equal to 5 × 10^{-6} sec, in good agreement with the measured value of 3 × 10^{-6} sec.[6]

(6) W. D. K. Clark, A. D. Litt, and C. Steel, *J. Amer. Chem. Soc.*, **91**, 5413 (1969).

(7) We established that γ deuteration does not occur by exchange of the biradical's hydroxyl proton with solvent followed by the normal reversion to ketone by observing absolutely no exchange in nonanophenone-γ,γ-d_2 recovered from prolonged irradiation in *tert*-butyl alcohol.

(8) R. D. Burkhart, *J. Amer. Chem. Soc.*, **90**, 273 (1968).

(9) (a) R. D. Burkhart, *J. Phys. Chem.*, **73**, 2703 (1969); (b) C. Sivertz, *ibid.*, **63**, 34 (1959).

(10) B. Smaller, J. R. Remko, and E. C. Avery, *J. Chem. Phys.*, **48**, 5174 (1968).

(11) H. G. Kuivila, *Accounts Chem. Res.*, **1**, 299 (1968).

(12) D. J. Carlson and K. U. Ingold, *J. Amer. Chem. Soc.*, **90**, 1055, 7047 (1968).

repress most back hydrogen transfer of the biradical,[13] τ_{BR} values under such conditions are probably several times longer than in hydrocarbon solvents, where reverse hydrogen transfer is the dominant reaction, and typical unsolvated τ_{BR} values may be more on the order of 10^{-7} sec. In fact, we have been unable to obtain any evidence that tributylstannane can trap the biradical obtained from irradiation of valerophenone in benzene. Because the stannane very rapidly reduces triplet ketones,[14] any trapping of the type II biradical would manifest itself as a quadratic Stern–Volmer plot for quenching of the type II reaction. No curvature is apparent in such a plot out to 0.7 M stannane, where 85% of the reaction is quenched. Moreover, valerophenone recovered from irradiation in the presence of tributyltin deuteride shows no incorporation of deuterium. From these observations we conclude that $\tau_{BR} < 2 \times 10^{-7}$ sec in benzene, in accord with our speculations regarding solvent effects.

If these type II biradicals actually live as long as 10^{-7} sec, the partial retention of optical activity noted in the cyclization of several ketones with asymmetric γ carbons[1,15] indicates β,γ bond rotation rates on the order of 10^8 sec^{-1}. Such a value is almost as slow as those estimated by Stephenson and Brauman in their stimulating discussion of 1,4 biradicals[16] and adds support to their contention that rates of triplet → singlet spin flips are not rate determining in the reactions of triplet-derived biradicals. These results can also be construed as lending support to the biradical mechanism for the thermal polymerization of styrene.[17]

Acknowledgment. This work was supported by several NSF grants.

[13] In low concentration, thiols enhance quantum yields, presumably by solvating the biradicals as alcohols do: P. J. Wagner and J. M. McGrath, *J. Amer. Chem. Soc.*, submitted for publication.

[14] P. J. Wagner, *ibid.*, **89**, 2503 (1967).

[15] (a) I. Orban, K. Schaffner, and O. Jeger, *ibid.*, **85**, 3033 (1963); (b) N. J. Turro and T. J. Lee, *ibid.*, **92**, 7467 (1970).

[16] L. M. Stephenson and J. I. Brauman, *ibid.*, **93**, 1988 (1971).

[17] W. A. Pryor and L. D. Lasswell, *Polym. Prepr.*, **11**, 713 (1970); **12**, 49 (1971).

[18] Alfred P. Sloan Fellow, 1968–1972.

Peter J. Wagner,[18] Richard G. Zepp
Chemistry Department, Michigan State University
East Lansing, Michigan 48823

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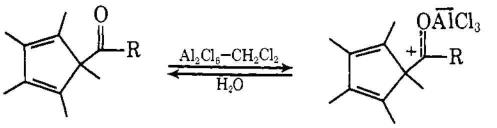
The Structure and Fivefold Degenerate Rearrangement of the 5-Acyl-1,2,3,4,5-pentamethylcyclopentadiene Aluminum Trichloride Complexes[1]

Sir:

The movement of the cyclopropyl ring around the periphery of the five-membered ring of a bicyclo[3.1.0]hexenyl cation is a recently described molecular rearrangement.[2] We wish to report here that 5-acylpentamethylcyclopentadienes react with anhydrous aluminum trichloride to form stable zwitterions. These complexes undergo a fivefold degenerate rearrangement which is directly comparable to that exhibited by the bicyclohexenyl cations except that the relative energies of the monocyclic and bicyclic structures have been completely reversed.

When a solution of either **1**, R = Me,[3] or **1**, R = Et[4] (1 equiv), in anhydrous CH_2Cl_2 was added to a solution of Al_2Cl_6 (1.1–1.4 equiv) in CH_2Cl_2 at −78°, a complex was rapidly formed.[5] These complexes were stable at +35° for long periods and could be decomposed with ice-water to recover the ketones in high yield. The pmr spectra of these complexes would strongly suggest that they can be represented as the zwitterions **2**.[6] The infrared spectra of the complexes support this structure in that the carbonyl absorption, originally at 1695 cm^{-1} in **1**, R = Me, had been shifted very considerably to lower frequency, *ca.* 1570 cm^{-1}.



1 **2**

While below −80°, the pmr spectrum of **2**, R = Me, consisted of four sharp singlets (Table I), on warming the solution, the three resonances attributable to the ring methyl groups broadened, coalesced at *ca.* −40°, and above this temperature became an averaged singlet. During this averaging, the C_6-methyl signal remained sharp and unchanged in position. The changes in the spectrum were completely reversed on cooling the sample.

This temperature dependence, which is very similar to that exhibited by σ-pentamethylcyclopentadienyl metal compounds,[7] apparently involves a migration of C_6 with its attendant substituents around the cyclopentadiene ring. Using a Saunders many-site nmr line-shape program,[8] line shapes were calculated and plotted for a series of rate constants and a good fit of calculated and observed spectra was obtained when the averaging was assumed to proceed by successive 1,5 shifts, that is, **2a**, R = Me $\rightleftharpoons$ **2b**, R = Me $\rightleftharpoons$ **2c**, R = Me, etc.[9] The rate constant of 26 sec^{-1} at −60°, obtained in this way, corresponds to a $\Delta F^{\ddagger}$ of 10.9 kcal/mol. Comparable temperature-dependent behavior was exhibited by **2**, R = Et, $\Delta F^{\ddagger}$ for its rearrangement being 9.7 kcal/mol.

[1] This work was supported in part by the National Research Council of Canada, and the Science and Engineering Division Research Board, McMaster University.

[2] D. W. Swatton and H. Hart, *J. Amer. Chem. Soc.*, **89**, 5075 (1967); R. F. Childs and S. Winstein, *ibid.*, **90**, 7146 (1968); R. F. Childs and B. Parrington, *Chem. Commun.*, 1540 (1970); V. A. Koptyug, L. K. Kuzubova, I. S. Isaev, and V. I. Mamatyuk, *ibid.*, 389 (1969); *Zh. Org. Khim.*, **6**, 2258 (1970); I. S. Isaev, V. I. Mamatyuk, L. I. Kuzubova, T. A. Gordymova, and V. A. Koptyug, *ibid.*, **6**, 2482 (1970); and P. Vogel, M. Saunders, N. Hasty, Jr., and J. A. Berson, *J. Amer. Chem. Soc.*, **93**, 1551 (1971).

[3] H. N. Junker, W. Schäfer, and H. Neidenbruck, *Chem. Ber.*, **100**, 2508 (1967).

[4] All the new ketones were prepared by reaction of the appropriate acid chloride with lithium pentamethylcyclopentadienide. Elemental analyses and spectroscopic data are fully in accord with the assigned structures.

[5] The Al_2Cl_6 used was purified by two sublimations, the second being carried out after admixture of the Al_2Cl_6 with aluminum powder. The CH_2Cl_2 was purified using the procedure of R. E. Jones and D. E. Wood, *J. Chem. Soc. A*, 1448 (1966). All manipulations were carried out in a drybox.

[6] The symmetry of the nmr spectra of these zwitterions could either be due to fast rotation, compared to the nmr time scale, around the C_5–C_6 bond, or, if rotation is slow, then the principal conformations are those that maintain the required plane of symmetry.

[7] A. Davison and P. E. Rakita, *Inorg. Chem.*, **9**, 289 (1970); Y. A. Ustynyuk, A. V. Kisin, and O. E. Oksinoid, *Zh. Obshch. Khim.*, **38**, 391 (1968); B. Floris, G. Illuminati, and G. Ortaggi, *Chem. Commun.*, 492 (1969); A. J. Ashe III, *J. Amer. Chem. Soc.*, **92**, 1233 (1970); F. A. Cotton and T. J. Marks, *ibid.*, **91**, 7523 (1969).

[8] M. Saunders, *Tetrahedron Lett.*, 1699 (1963).

[9] R. B. Larrabee, *J. Amer. Chem. Soc.*, **93**, 1510 (1971).