On the other hand, nucleophilic solvent participation into a developing carbocation center is the intermolecular counterpart of intramolecular neighboring group participation. The latter, in accordance with the general concept of carbocation behavior in electrophilic interactions,[5] can be by an n-donor group (such as halogen), a π donor (as in the cyclopentenylethyl route to the norbornyl cation), or a σ donor (the C.1–C.6 bond in forming the ion from norbornyl precursors). There can be competition between inter- and intramolecular nucleophiles, as, for example, recently discussed by Nordlander in solvolytic studies in trifluoroacetic acid.[23] All this, however, does not affect the structural conclusions reached concerning the norbornyl ion, which in my view finally ends the so-called "nonclassical ion controversy".[11]

Nonclassical carbonium ions containing two-electron, three-center bonded carbocation centers are now firmly proven to exist also as long-lived species. The differentiation of these ions from trivalent classical carbenium ions served a most useful purpose in defining these differing carbocations.[47] However, there always exists a continuum of charge delocalization depending on the characteristics of specific systems (comprising both inter- and intramolecular interactions).

The mode of charge delocalization in my view is a continuous process, with faster electronic movement being followed by slower nuclear reorganization.[4] There is, however, no reason to believe in a dichotomy of these processes, as once suggested by Traylor in his "vertical stabilization" concept.[48,49]

The "classical–nonclassical ion controversy" is brought to conclusion not only by overwhelming chemical and structural evidence, but also by consideration of our present day understanding of chemical bonding and charge delocalization. Simply, there is no such thing as a completely "classical" type of carbocation. Charge is always delocalized to a significant degree whenever an electron-deficient center is formed in a molecule. Whether this happens through π-, n-, or σ-electron-pair interactions and to what a degree is dependent of the specific system, but not of principle. The norbornyl cation is only one of the many carbocations showing C–C σ-bond delocalization, and will be remembered in years to come as an interesting but by no means unique member of a substantial class of compounds.

Rather than being rare, the two-electron, three-center bond is characteristic of electron-deficient molecules, including nonclassical carbocations. The real significance of the nonclassical norbornyl cation is, however, that it provides evidence for the close similarity of intramolecular σ- and π-bond donor ability. Extending the same principle to intermolecular interactions raised the question as to whether σ-bond donor ability is a general phenomenon in organic chemistry. Our work since affirmed it, and has led to a rapid development of the reactions of saturated hydrocarbons with electrophiles.[4] Pentacoordinated carbonium ions, closely related in nature to the norbornyl cation, of which the methonium ion (CH_5^+) is parent, represent the key to all these reactions.[5,6]

(47) G. A. Olah, *J. Am. Chem. Soc.*, **94**, 808 (1972).
(48) T. G. Taylor, W. Hanstein, H. J. Berwin, N. A. Clinton, and R. S. Brown, *J. Am. Chem. Soc.*, **93**, 5715 (1971).
(49) G. A. Olah and G. Liang, *J. Am. Chem. Soc.*, **97**, 1920 (1975).

Thione Photochemistry, and the Chemistry of the S_2 State[1]

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The study of the photochemistry of the carbonyl group dates from the earliest period of investigation of photic interactions with organic substances; that is, about the turn of the century. In contrast, the first study of a thiocarbonyl compound appears to have been reported in the thirties, and no systematic investigations were initiated until the late sixties.

The lack of interest may be variously interpreted. Certain thiones and thials have intimidating olefac-

tory qualities;[2] they have ground states that are very reactive,[3] leading to the formation of dimers, trimers, or polymers; and those substances having an α hydrogen have a strong tendency to thioenolize. These undesirable characteristics are not possessed by all members of the group, however. In the last 8 years or so, it has become clear that the excited thione function has distinctive characteristics of its own, perhaps

Paul de Mayo was born and educated in London. He took his Ph.D. at London University with Sir Derek Barton, whom he followed as lecturer to Birkbeck, Glasgow, and Imperial College. In 1959, he moved to the University of Western Ontario where, in 1968, he founded the Photochemistry Unit. His research interests include photochemistry, flash thermolysis, and the chemistry of reactive small molecules.

(1) Photochemical Synthesis, 62. Publication No. 138 from the Photochemistry Unit, University of Western Ontario.
(2) E. Baumann and E. Fromm, *Ber.*, **22**, 2592 (1889); much, if not all, of the vile odor associated with thiocarbonyl compounds is to be attributed to impurities.
(3) For instance thioacrolein has recently[4] been prepared by flash thermolysis and is reactive even at the temperature of liquid nitrogen. Thiobenzaldehyde[4] is stable up to about −140°.

the single most important being *the frequent, if not general, ability of the excited thione to give products derived from reaction of a higher singlet state.*[5]

This Account will be limited to simple aromatic and aliphatic thiones from whose study most mechanistic information[6] is available.

Spectroscopy

All thiocarbonyl compounds show a long-wavelength absorption band which has been attributed to a $\pi^* \leftarrow n$ transition.[7] With saturated substances this occurs near 500 nm (orange-pink) ($\epsilon \sim 10$); with conjugation this moves closer to 600 nm (blue) ($\epsilon \sim 100$). In addition, on the long-wavelength side of this absorption band there may be a smaller band which has been attributed[7a,8] to a $T_1 \leftarrow S_0$ transition. The energies of the lowest, n,π^*, singlet of the thiones vary from approximately 56 (alicyclic) to 44 kcal/mol (aromatic). No fluorescence from this state in thiones has yet been reported.

All thiones so far examined phosphoresce,[7a,9] and the n,π^* singlet–triplet separation is small.[7a] The lifetimes in a matrix are one to two orders of magnitude shorter than those of the corresponding ketones.[10] Lifetimes have also been determined in fluid solution by laser flash photolysis. Decay occurred in solution by first-order kinetics, and the derived reciprocal of the unimolecular decay constants for thiobenzophenone, Michler's thione, and adamantanethione were 1.4,[11] 0.7,[11] and 1.4[12] × 10^{-6} sec. Quenching of the triplet by ground-state thione was observed, and the bimolecular quenching constant was close to that to be expected for control by diffusion.[13] This should be contrasted with carbonyl self-quenching rates which, for benzophenone, depending on the solvent[15] and the method, appear to be from 1.3 × 10^5 to 3.25 × 10^5 M^{-1} sec^{-1}.[16] In neither system is the precise mode of self-quenching known. The formation of a 1,3-dithietane (and the marked ineffi-

ciency of the process) in the case of adamantanethione (*vide infra*) may be relevant.[17]

At shorter wavelengths thiones show high-intensity bands, and it seems likely that that lower in energy is π,π^*. The energy separation from the S_1 level is large, in the region of 40–50 kcal/mol.[18-21] This is comparable with that in azulene which has an exceptionally long S_2 lifetime.[22] The lifetimes of thiones in the S_2 state ($\sim 10^{-10}$–10^{-11} sec) are long enough to permit both inter- and intramolecular reactions to occur from this state.

In the case of aliphatic and alicyclic thiones there is another band overlapping at somewhat higher energy which may be $\sigma^* \leftarrow n$.[21]

Recently it has been found that aralkyl thiones emit from S_2 in solution ($\Phi_F = 0.05$). This has permitted a direct, but approximate, determination of the lifetime which is ~ 400 psec,[20] in acceptable agreement with that obtained from the quenching studies to be described below. No emission was observed from S_1.[23]

Aromatic Thiones

The first record of the study of an aromatic thione is that of Schönberg and Mustafa[24] who were concerned with the photooxidation of several substituted aromatic thiones. This was followed, in 1962,[25] by a preliminary study of both the photochemical oxidation and reduction of thiobenzophenone. This work contained the first report that there was wavelength dependence in the solution photochemistry of a thione.

Cycloaddition. In 1964, Kaiser and Wulfers[26] reported that irradiation of thiobenzophenone at 254 nm in the presence of 1-hexene or 2-butene produced olefins presumed to be formed by decomposition of intermediate, but unisolated, thietanes (Scheme I). Irradiation through Pyrex was reported as not affording a product,[27] again suggesting a wavelength dependence. Subsequent studies by another group[30] re-

(4) H. G. Giles, R. A. Marty, and P. de Mayo, *J. Chem. Soc., Chem. Commun.*, 409 (1974).

(5) For discussions of the very limited conjugated carbonyl photochemistry in solution involving higher states see: J. Gloor and K. Schaffner, *Helv. Chim. Acta*, 57, 1815 (1974); S. Hirayama, *Rev. Phys. Chem. Jpn.*, 42, 49 (1972). Reactions in the gas phase from higher states—unimolecular processes—are commonplace.

(6) P. de Mayo, *Acc. Chem. Res.*, 4, 41 (1971), ref 10.

(7) (a) For a review, see: D. S. L. Blackwell, C. C. Liao, R. O. Loutfy, P. de Mayo, and S. Paszyc, *Mol. Photochem.*, 4, 171 (1972); (b) S. D. Gupta, M. Chowdhury, and S. C. Bera, *J. Chem. Phys.*, 53, 1293 (1970); M. J. Janssen, *Recl. Trav. Chim. Pays-Bas*, 79, 464 (1960); H. McConnell, *J. Chem. Phys.*, 20, 700 (1952); J. Fabean and R. Mayer, *Spectrochim. Acta*, 20, 299 (1964); W. A. Lees and A. Burawoy, *Tetrahedron*, 20, 1533 (1964); J. Fabean, H. Viola, and R. Mayer, *ibid.*, 23, 4323 (1967); P. Brocklehurst and A. Burawoy, *ibid.*, 10, 118 (1960).

(8) C. A. Emeis and L. J. Oosterhoff, *J. Chem. Phys.*, 54, 4809 (1971).

(9) G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.*, 67, 994 (1945); G. N. Lewis and M. Kasha, *ibid.*, 66, 2100 (1944).

(10) Quenching of the excited state by the ground-state thione (vide infra) is undoubtedly occurring under these conditions.

(11) D. R. Kemp and P. de Mayo, *J. Chem. Soc., Chem. Commun.*, 233 (1972).

(12) A. H. Lawrence, P. de Mayo, R. Bonneau, and J. Joussot-Dubien, *Mol. Photochem.*, 5, 361 (1973).

(13) In the case of adamantanethione, preliminary kinetic studies had already revealed the existence of an efficient self-quenching process.[14]

(14) C. C. Liao and P. de Mayo, *Chem. Commun.*, 1525 (1971).

(15) In water a value for k_{sq} of 10^8 M^{-1} sec^{-1} has been reported: M. B. Ledger and G. Porter, *J. Chem. Soc., Faraday Trans. 1*, 3, 539 (1972).

(16) D. I. Schuster and T. Weil, *J. Am. Chem. Soc.*, 95, 4091 (1973). The importance of self-quenching in $^3\pi,\pi^*$ systems has long been recognized: O. L. Chapman and G. Wampfler, *J. Am. Chem. Soc.*, 91, 5390 (1969); see also P. S. Engel and B. M. Monroe, *Adv. Photochem.*, 8, 245 (1971); C. D. DeBoer and R. H. Schlessinger, *J. Am. Chem. Soc.*, 94, 656 (1972).

(17) Yang has considered 1,3-dioxetane formation as one of the possibilities for the explanation of observations of self-quenching and isotope exchange in acetone: N. C. Yang, W. Eisenhardt, and J. Libman, *J. Am. Chem. Soc.*, 94, 4030 (1972).

(18) P. de Mayo and H. Shizuka, *J. Am. Chem. Soc.*, 95, 3942 (1973).

(19) P. de Mayo and R. Suau, *J. Am. Chem. Soc.*, 96, 6807 (1974).

(20) M. H. Hui, P. de Mayo, R. Suau, and W. R. Ware, *Chem. Phys. Lett.*, 31, 257 (1975).

(21) K. J. Rosengren, *Acta Chem. Scand.*, 16, 2284 (1962).

(22) Azulene has $\tau = 1.4 \times 10^{-9}$ sec (I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules", 2nd ed, Academic Press, New York, N.Y., 1971). For an expression of the energy gap law, see, for example, R. Engleman and J. Jortner, *Mol. Phys.*, 18, 145 (1970).

(23) Recently Steer and Knight have reported that thiophosgene emits from S_2, but only from certain vibrational levels: S. Z. Levine, A. R. Knight, and R. P. Steer, *Chem. Phys. Lett.*, 29, 73 (1974). [Emission from S_1 had been previously observed: J. R. McDonald and L. E. Brus, *Chem. Phys. Lett.*, 16, 587 (1972).] Xanthione has very recently been reported to emit from S_2: J. R. Huber and M. Mahaney, *Chem. Phys. Lett.*, 30, 410 (1975).

(24) A. Schönberg and A. Mustafa, *J. Chem. Soc.*, 275 (1943).

(25) G. Oster, L. Citarel, and M. Goodman, *J. Am. Chem. Soc.*, 84, 703 (1962).

(26) E. T. Kaiser and T. F. Wulfers, *J. Am. Chem. Soc.*, 86, 1897 (1964).

(27) By irradiation at $\lambda > 4300$ nm[28] we have isolated in low quantum yield in the hexene case the intermediate thietane. Irradiation at 254 nm of the thietane then gave 1,1-diphenylethylene and 1,1-diphenylhex-1-ene (contrast ref 29).

(28) P. de Mayo and A. A. Nicholson, *Isr. J. Chem.*, 20, 341 (1972).

(29) G. Tsuchihashi, M. Yamauchi, and M. Fukuyama, *Tetrahedron Lett.*, 1971 (1967).

(30) Y. Yamada, M. Yoshioka, and N. Sugiyama, *J. Org. Chem.*, 33, 1240 (1968); Y. Omote, M. Yoshioka, K. Yamada, and N. Sugiyama, *ibid.*, 32, 3676 (1967). Other conjugated systems have since been studied with similar results: T. S. Cantrell, *ibid.*, 39, 853 (1974).

Scheme I[a]

$a\ \phi = C_6H_5$.

Scheme II

Scheme III

Scheme IV
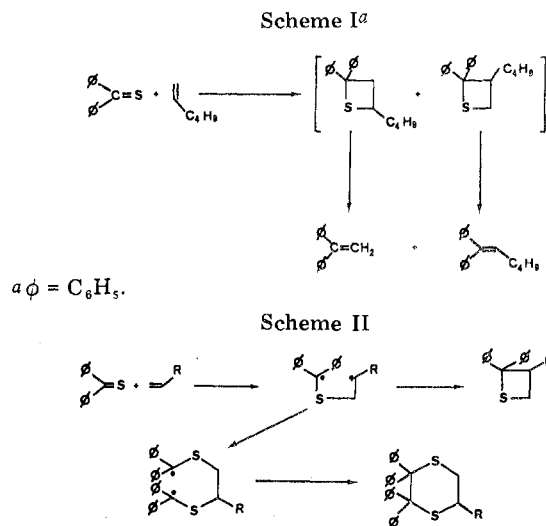
ported the formation of adducts between dienes and thiobenzophenone excited in the S_1 band: both 1,2 and 1,4 adducts were reported. Simultaneously, an extended series of papers by Tsuchihashi, Ohno, and their collaborators appeared. It was shown that with olefins substituted by other than electron-withdrawing groups, either thietanes or 1,4-dithianes could be obtained (Scheme II)[29,31,32] on excitation into both S_1 and S_2. It was assumed, in the absence of quenching or sensitizing experiments, that the reaction proceeded through the lowest triplet. Supporting this assumption was the observation of the occurrence of isomerism in the recovered olefin which, since energy transfer was excluded, suggested a biradical intermediate. Whether the dithiane or thietane was formed depended both on the specific olefin and the concentration of thione, and was believed to be a consequence of the efficient radical-trapping abilities of thiobenzophenone.[33] Aside from this latter feature, the mechanism paralleled in many ways that proposed for oxetane formation via the n,π^* triplet.[34] The reaction has been extended to allenes.[35,36] In the case of electron-deficient olefins it was originally reported that excitation into S_1 led to no reaction.[32] Later, it was found that with thiobenzophenone and acrylonitrile, the 1,4-dithiane was formed, but in very low quantum yield.[28,37] In addition a formal Diels–Alder type of reaction was observed,[28,37] which has also been reported for allenes[35,36] and acetylenes[38,39] (Scheme III). This reaction does not require electron-withdrawing substituents since it has been observed with tetramethylethylene.[28] The reaction may also occur thermally.[36]

The suggestion of Kaiser and Wulfers[26] as regards wavelength dependence was confirmed by Ohno,

(31) A. Ohno, Y. Ohnishi, M. Fukuyama, and G. Tsuchihashi, *J. Am. Chem. Soc.*, **90**, 7038 (1968).

(32) A. Ohno, Y. Ohnishi, and G. Tsuchihashi, *J. Am. Chem. Soc.*, **91**, 5038 (1969); A. Ohno, Y. Ohnishi, and G. Tsuchihashi, *Tetrahedron Lett.*, 283 (1969).

(33) G. Tsuchihashi, M. Yamauchi, and A. Ohno, *Bull. Chem. Soc. Jpn.*, **43**, 968 (1970).

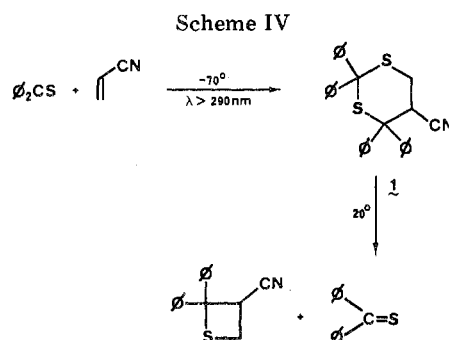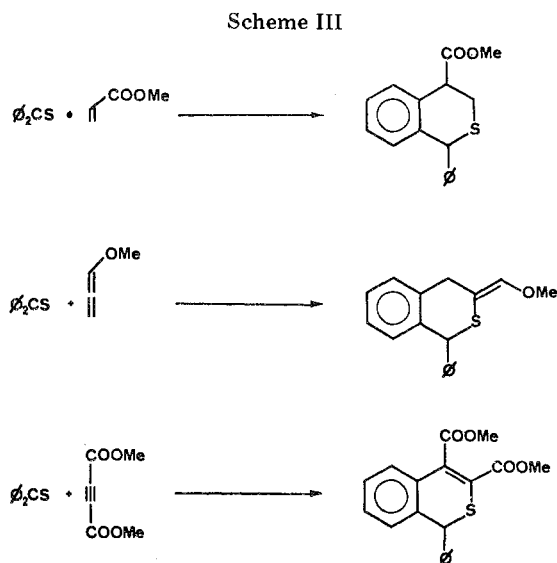(34) D. R. Arnold, *Adv. Photochem.*, **6**, 301 (1968).

(35) H. Gotthardt, *Tetrahedron Lett.*, 2345 (1971).

(36) H. Gotthardt, *Chem. Ber.*, **105**, 2008 (1972); H. Gotthardt, *ibid.*, **107**, 1856 (1974).

(37) P. de Mayo and H. Shizuka, *Mol. Photochem.*, **5**, 339 (1973).

(38) A. Ohno, T. Koizumi, Y. Ohnishi, and G. Tsuchihashi, *Tetrahedron Lett.*, 2025 (1970).

(39) A. Ohno, T. Koizumi, and Y. Ohnishi, *Bull. Chem. Soc. Jpn.*, **44**, 2511 (1971).

Tsuchihashi, and their collaborators,[32,40] when they observed that thiobenzophenone excited into S_2 added rapidly to olefins substituted by electron-withdrawing groups. The addition gave, at room temperature, the thietane, and was stereospecific. It was presumed that the π,π^* singlet was involved. Other examples have been provided by Gotthardt.[36]

The reaction has been investigated in detail in a single system (thiobenzophenone–acrylonitrile). The result may be compared with that following S_1 activation. Although at room temperature the thietane is obtained, excitation into S_2 at $-70°C$ (See Scheme IV) leads to the formation of a 1,3-dithiane (1); this has been isolated. At room temperature it decomposes in high yield to thietane and thiobenzophenone. It has thus been assumed that the 1,3-dithiane is an intermediate in the room-temperature process; this is supported by a kinetic study which requires the participation of ground-state thione. The quantum yield of formation of thietane found is expressed by eq 1 where k_1 is the unimolecular rate constant for decay of the excited species, k_2 is the bimolecular rate constant for reaction with acrylonitrile (A), and k_3 is the bimolecular rate constant for the self-quenching process indicated in eq 2.

$$\Phi = \frac{k_2[A]}{k_1 + k_2[A] + k_3[S]} f(S) \qquad (1)$$

$$S_2 + S_0 \rightarrow S_1 + S_0\ (\rightarrow 2S_0) \qquad (2)$$
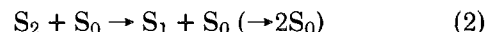
Equation 1 contains the term $f(S)$ (see ref 18), indicating that the quantum yield also has a depen-

(40) A. Ohno, Y. Ohnishi, and G. Tsuchihashi, *Tetrahedron Lett.*, 161 (1969).

<table>
<tr><td align="center">Scheme V</td><td align="center">Scheme VI</td></tr>
</table>
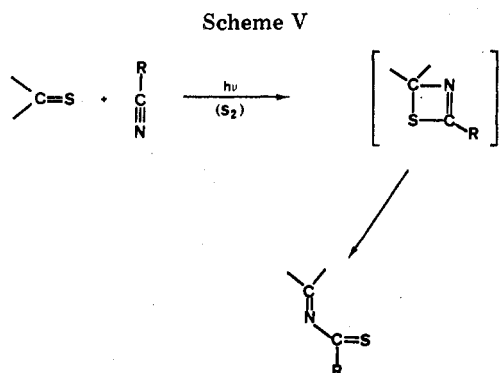
dence on [S] aside from that implied in the term $k_3[S]$. This term derives from the interaction of complexes with S_0. The reciprocal of the function $f(S)$ appears to be linear and varies directly with thione concentration. It is this function which is responsible for the observed *decrease* in quantum yield for thietane formation with *increased* thione conce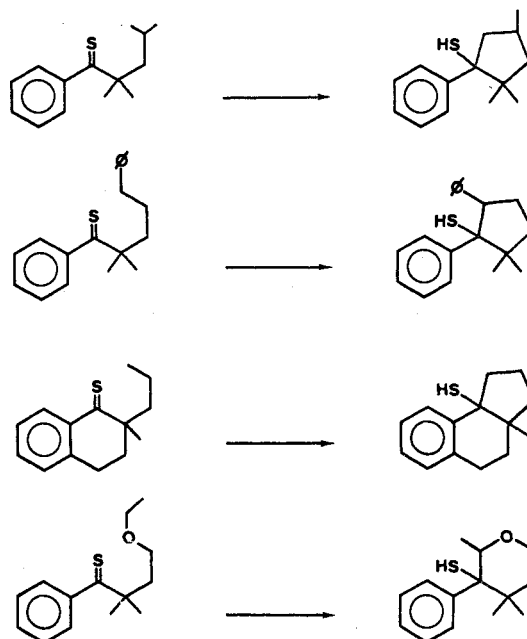ntration, more so than the $k_3[S]$ term as was first assumed.[41] The behavior of $f(S)$ requires that decay of a triple complex, to 1,3-dithiane or starting materials, both with and without the intervention of another thione molecule occur.[42] The complexes here postulated involve *a higher state of the excited species*. The excited species responsible for the reaction, and which is generated by excitation into S_2, is quenched by biacetyl giving, assuming diffusion-controlled quenching, a lifetime of 5×10^{-11} sec.

Thietane formation with olefins with electron-withdrawing groups is stereospecific.[32,36] There is a lack of regiospecificity in the addition to crotononitrile (2:1 ratio), but that to acrylonitrile appears to be regiospecific.

Other cycloadditive properties of the aromatic thione in a higher excited state have been noted. A general reaction, which does not proceed from S_1 or T_1, is the addition to the nitrile function (Scheme V). To date this appears to be the only known addition of an excited molecule to the nitrile function. It occurs with thiobenzophenone and aralkyl and alicyclic thiones.[43] The final product of the addition is not the four-membered ring but the ring-opened electrocyclic isomer.

Hydrogen Abstraction by Aromatic Thiones. The first system to be examined was that of the reaction of thiobenzophenone with alcohols and cyclohexane. A wavelength dependence of disappearance of thione was noted, the reaction with cyclohexane by excitation into S_1 being extremely slow.[25] This latter observation has been confirmed recently.[44a] It has also been shown that abstraction of hydrogen by the aromatic thione excited into S_1 requires that the C–H bond be weakened by substitution whether the reac-

tion be intramolecular[45] or intermolecular.[44] Activation may be by oxygen substitution[44,45] or the introduction of unsaturation.[46-48] The intramolecular reaction occurs at the γ position and it has been presumed that this is a triplet (n,π^*) reaction.

Excitation into S_2 leads to different results. Intramolecularly five-membered rings are obtained, which has led to the view that this may be a concerted $(_\pi2 + _\sigma2)$ reaction. The δ C–H is conformationally best placed for interaction in the $\pi(\pi^*)$ volume of space.[45] This reaction has been used for a synthesis of the terpenoid cuparene.[49] Blocking the δ position with oxygen leads to ϵ and γ insertion and the formation of four- and six-membered rings. The absence of either ϵ or γ hydrogen (or steric encumbrance) leads to no reaction.[50] The state(s) immediately responsible for cyclobutanethiol formation in oxygen-containing chains is presently uncertain.

Biacetyl quenching[50] in a nonoxygenated compound indicated that the reactive species is S_2 or derived from it and confirms the lifetimes determined from fluorescence measurements. The lack of quenching by over 2 M piperylene together with the quantum yield of formation $(\Phi = 0.03)$ excludes a triplet higher in energy than piperylene (or, less likely, requires a rate constant greater than 10^{10} sec^{-1}). The lack of product formation on sensitization appears to exclude a triplet between T_1 and $\sim$55 kcal. The reaction therefore proceeds via S_2. It is possible that the products of irradiation of thiobenzophenone in cyclohexane (Pyrex) may be derived by a similar insertion process. The reported products (including products of overirradiation) are diphenylcyclohexyl sulfide, diphenylcyclohexylmethane, sulfur, and dibenzhydryl sulfide and disulfide (in yields of 37, 8, 18, 10, and 11%, respectively). The products of irra-

(41) R. S. H. Liu and V. Ramamurthy, *Mol. Photochem.*, **3**, 261 (1971).

(42) The participation of complexes in reaction with other molecules appears established: see, for instance, R. O. Campbell and R. S. H. Liu, *Mol. Photochem.*, **6**, 207 (1974); J. Saltiel and D. E. Townsen, *J. Am. Chem. Soc.*, **95**, 6140 (1973); P. P. Wells and H. Morrison, *ibid.*, **97**, 154 (1975). The existence of triple complexes also seems secure: for example, H. Beens and A. Weller, *Chem. Phys. Lett.*, **2**, 140 (1968); J. K. Roy, F. A. Carroll, and D. G. Whitten, *J. Am. Chem. Soc.*, **96**, 6349 (1974); R. A. Caldwell, D. Creed, and H. Ohta, *ibid.*, **97**, 3246 (1975), and references there cited.

(43) D. S. L. Blackwell, P. de Mayo, and R. Suau, *Tetrahedron Lett.*, 91 (1974).

(44) (a) A. Ohno and N. Kito, *Int. J. Sulfur Chem., Part A*, **1**, 26 (1971); (b) N. Kito and A. Ohno, *Bull. Chem. Soc. Jpn.*, **46**, 2487 (1973).

(45) P. de Mayo and R. Suau, *J. Am. Chem. Soc.*, **96**, 6807 (1974).
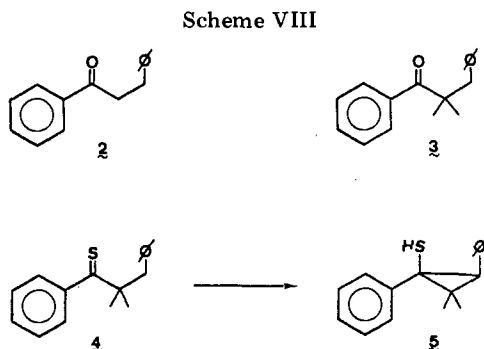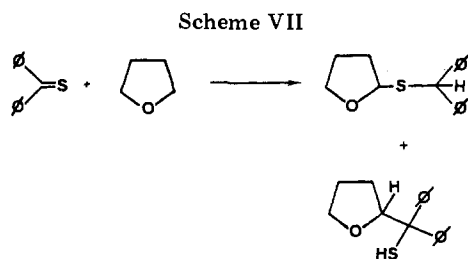
(46) Y. Ohnishi and A. Ohno, *Bull. Chem. Soc. Jpn.*, **46**, 3868 (1973).

(47) N. Kito and A. Ohno, *Chem. Commun.*, 1338 (1971); N. Kito and A. Ohno, *Int. J. Sulfur Chem.*, **8**, 427 (1973).

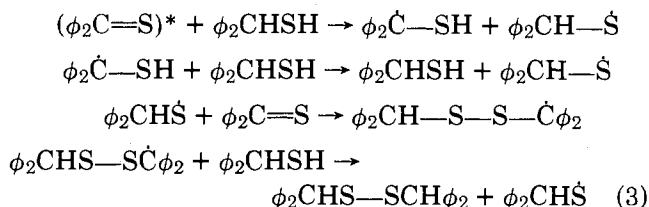(48) M. Hoshino and A. Couture, unpublished observations.

(49) P. de Mayo and R. Suau, *J. Chem. Soc., Perkin Trans. 1*, 2559 (1974).

(50) R. Suau and M. Hoshino, manuscript in preparation.

Scheme VII

Scheme VIII

Scheme IX

diation of thiobenzophenone (S_2) in the presence of tetrahydrofuran and diethyl ether (see Scheme VII) are also those that would be predicted on this basis, and make up 90 and 87% of the material, respectively;[51] but the presence of an oxygen atom makes this less certain and charge-transfer processes are not excluded.

The reduction of thiobenzophenone has also been studied in the special case where the hydrogen donor is the more powerful reducing agent, the corresponding thiol, benzhydrylthiol. In this case reaction proceeded by excitation into S_1, and the main product was the disulfide.[44a] An economic description is:

$$(\phi_2 C{=}S)^* + \phi_2 CHSH \rightarrow \phi_2 \dot{C}{-}SH + \phi_2 CH{-}\dot{S}$$

$$\phi_2 \dot{C}{-}SH + \phi_2 CHSH \rightarrow \phi_2 CHSH + \phi_2 CH{-}\dot{S}$$

$$\phi_2 CH\dot{S} + \phi_2 C{=}S \rightarrow \phi_2 CH{-}S{-}S{-}\dot{C}\phi_2$$

$$\phi_2 CHS{-}S\dot{C}\phi_2 + \phi_2 CHSH \rightarrow$$
$$\phi_2 CHS{-}SCH\phi_2 + \phi_2 CH\dot{S} \quad (3)$$

Since the chain is initiated by the formation of thiyl radical, it is not surprising that the disulfide is also produced thermally. The mechanism is supported by analogy with the similar reduction of adamantanethione discussed below.

Intramolecular abstraction of hydrogen by an excited aromatic ketone occurs in the γ and occasionally, if conformational preferences require it, in the δ position. The ketone **2** (Scheme VIII) is, for instance, photochemically stable,[52] while **3** undergoes only a

(51) In these irradiations[44b] radicals of type ii were detected by ESR

i   ii
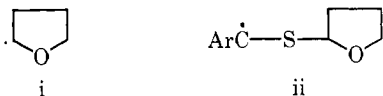
spectroscopy. Their detection implies some passage via i, the radical then being trapped by the thiobenzophenone, but it need not indicate the main path. In addition, the preparative irradiation appears to have been carried out through Pyrex and the ESR determination in quartz. Alternatively, the radicals may be derived from a charge-transfer process from S_2.

(52) F. R. Stermitz, D. E. Nicodem, V. P. Muralidharan, and C. M. O'Donnell, *Mol. Photochem.*, **2**, 87 (1970). This compound is deactivated, with regard to intermolecular photoreduction, by a not well-understood process; see also P. J. Wagner, P. A. Kelso, A. E. Kemppainen, A. Haug, and D. R. Graber, *ibid.*, **2**, 81 (1970); D. G. Whitten and W. E. Punch, *ibid.*, **2**, 77 (1970).
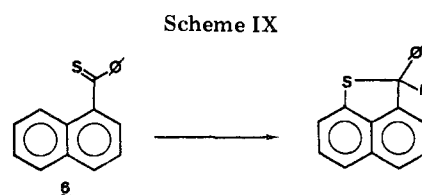
slow type I fission. In the absence of γ hydrogen, and in the presence of an adjacent nitrogen atom, β abstraction has been occasionally observed,[53] but not, apparently, in simple systems. The thione **4**, on the other hand, excited into S_1, is smoothly converted to the cyclopropyl derivative **5**.[54] It may be that the ketones are apparently unreactive because of reversible addition to the benzene ring, but such a pathway should be available to the thione also since products of related additions are known.[55,56] An alternative explanation is that the increased size of the nonbonding 3p (as against 2p) orbital—approximately double—merely renders the β insertion stereochemically more facile.

Cyclization. The multiplicity of the species undergoing reaction following excitation to S_1, has, in most cases, not been established, but has been assumed to be the triplet. One reaction has been reported, however, which appears to proceed through the singlet.[56]

This reaction is the photocyclization of thiobenzoyl derivatives of aromatic hydrocarbons having a peri position vacant adjacent to the substituent. The products are thiophane derivatives. The cyclization of **6** is illustrative (see Scheme IX). The reaction occurs with alternant hydrocarbons, but apparently fails with nonalternant hydrocarbons. The mechanism has been studied in more detail in the case of **6**.

The reaction is inefficient ($\Phi \sim 10^{-3}$). It is not quenched by triplet quenchers of sufficiently low energy, yet it has been shown, by monitoring the triplet generated by laser flash photolysis, that this species is quenched under such conditions. In the presence of D_2O the benzylic proton is replaced by deuterium. Although other mechanisms are imaginable, passage through the singlet is simplest.

Alicyclic Thiones

Cycloaddition. Although other simple thiocarbonyl derivatives have been reported to undergo dimerization[57] or cycloaddition,[58] the only mechanistic study so far undertaken is that of adamantanethione.

The first report[14] described the addition of the thione, following excitation into S_1, to α-methylstyr-

(53) A. Padwa and R. Gruber, *J. Am. Chem. Soc.*, **92**, 107 (1970); A. Padwa and W. Eisenhardt, *ibid.*, **93**, 1400 (1971); H. J. Roth and M. H. El Raie, *Tetrahedron Lett.*, 2445 (1970). The process is implicated, also, in the photoenolization of aromatic diketones: R. G. Zepp and P. J. Wagner, *J. Am. Chem. Soc.*, **92**, 7466 (1970).

(54) M. Hoshino and A. Couture, unpublished observations. For an example of indirect cyclopropanol formation, see E. C. Alexander and R. J. Jackson, *J. Am. Chem. Soc.*, **96**, 5663 (1974).

(55) P. de Mayo and H. Y. Ng, *Tetrahedron Lett.*, 1561 (1973).

(56) R. Lapouyade and P. de Mayo, *Can. J. Chem.*, **50**, 4068 (1972); A. Cox, D. R. Kemp, R. Lapouyade, P. de Mayo, J. Joussot-Dubien, and R. Bonneau, *Can. J. Chem.*, in press.

(57) J. J. Worman, M. Shen, and P. C. Nichols, *Can. J. Chem.*, **50**, 3923 (1972); U. Schmidt, K. Kabitzke, I. Boie, and C. Osterroht, *Ber.*, **98**, 3819 (1965); A. Schönberg, A. Stephenson, *ibid.*, **66**, 567 (1933); W. J. Middleton, E. G. Howard, and W. H. Sharkey, *J. Org. Chem.*, **30**, 1375 (1965).

(58) H. Gotthardt, *Tetrahedron Lett.*, 1221 (1973); H. Gotthardt and M. Listl, *ibid.*, 2849 (1973); C. Fombert, J. L. Fourrey, P. Jouin, and J. Moron, *ibid.*, 3007 (1974); J. L. Fourrey, P. Jouin, and J. Moron, *ibid.*, 3229 (1973); J. L. Fourrey, P. Jouin, and J. Moron, *ibid.*, 3005 (1974).
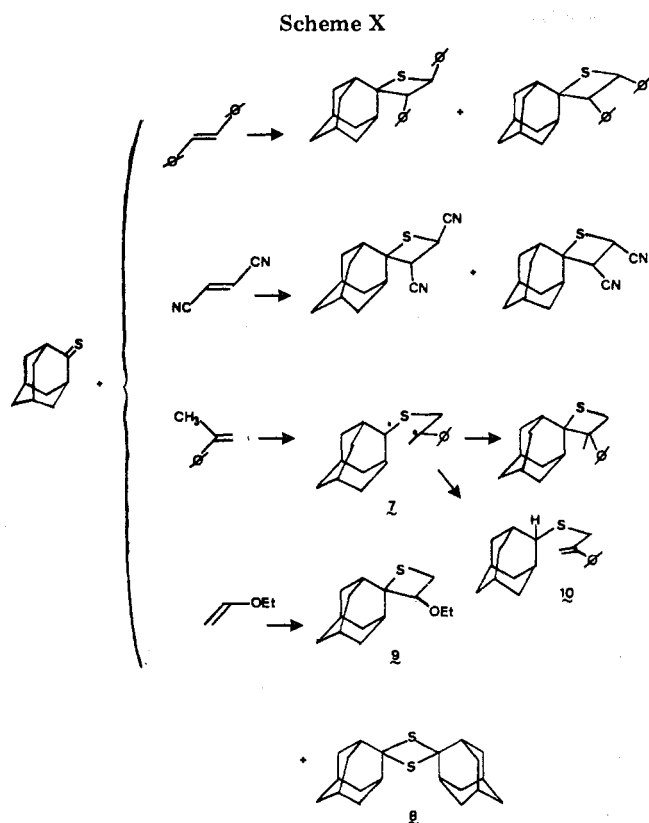
Scheme X

ene, ethyl vinyl ether, 1,1-diphenylethylene, *trans*-stilbene, and fumaronitrile. In all cases a thietane was obtained (Scheme X). In addition, in the case of α-methylstyrene, an open-chain product of addition was isolated (10), strongly suggesting the formation of an intermediary 1,4 biradical (7) in which a hydrogen transfer had occurred. The intramolecular nature of the transfer was shown by the nonformation of cross-products on irradiating the thione in the presence of a trideuteriomethyl- and triprotiomethylstyrene mixture.

With fumaronitrile and stilbene as olefins, stereoisomeric products were formed. In both cases the starting olefin was, after completion of the reaction, found to be isomerized, although only in the stilbene case is triplet-energy transfer from the thione exothermic. With ethyl vinyl ether the reaction was regiospecific,[59] as it was with acrylonitrile.[60] The product, **9**, is that expected from the more stable biradical intermediate. A product accompanying all cycloadditions was the dimer, **8**.

The addition to ethyl vinyl ether ($\Phi \sim 10^{-4}$) and to acrylonitrile could be sensitized,[16] and, under conditions where the sensitizer triplet could be quantitatively trapped, the sensitized quantum yield was that of the direct reaction. This indicated a triplet pathway and suggested that the intersystem crossing efficiency in the thione was close to unity. Similar observations have been made for the dimerization.[60]

The addition, both to ethyl vinyl ether and to acrylonitrile, and also the dimerization could be quenched[14,60] with a variety of triplet quenchers, all, except cyclooctatetraene, at a near diffusion-controlled rate. It could be concluded that the reaction proceeded through the $^3(n,\pi^*)$ state.

The quantum yield of addition depended not only on the concentration of olefin but, inversely, on the thione concentration.[16] This was not surprising in view of the simultaneous formation of dimer, but the original study suggested a very high rate constant for quenching of the thione triplet by ground-state thione ($>10^9$ M^{-1} sec^{-1}). Later, flash photolytic studies[12] showed that the quenching was near diffusion controlled. With this information, the rate constant for reaction of thione triplet with olefin could be extracted ($\sim10^8$ M^{-1} sec^{-1}).[60] Since the quantum yield of dimer formation is also minuscule, it was apparent that the low quantum yields in both cycloaddition and dimerization ($\Phi_{dim} \sim 10^{-4}$) were not due to low rate constants, but to inefficient product formation by the trapped triplet.

Such an inefficiency occurs in other cycloadditive processes such as oxetane formation[34] and enone cycloaddition, and indicates the decay to ground state of one or more intermediates. Usually in the reactions named, the inefficiency is less than one order of magnitude, whereas here it is between two and three. The inefficiency in the thione dimer formation is such that only one in ~7000 of the triplets quenched leads to product. In triplet cycloadditions an intermediate is frequently identified with a biradical, and its collapse to starting materials may be one of the sources of inefficiency. Such a biradical, **7** (type B), is required in the formation of **10**.

The only evidence presently available concerning the closure of thiatetramethylenes does not lead to the expectation of such a reluctance to close. Thus, the singlet and triplet species derived by sensitized or direct photolysis of 3-ethyl-2-propylthietane have lifetimes sufficient for bond isomerization and appear to generate the olefin or close to the thietane with comparable efficiencies,[61] that is, within an order of magnitude. The biradical (type A) is related to that (type C) involved in dimer formation. Yet, the difference in efficiency in closure of A and C is required to be two orders of magnitude. This may be an indication that the major part of this inefficiency arises in some *other* biradical formation, or *before*

A   B   C

biradical formation, in the decay of a triplet excimer (dimerization) or exciplex (cycloaddition).

Reaction from S₂. Excitation of adamantanethione into S_2 in the presence of ethyl vinyl ether also leads both to dimer and thietane formation, but in greatly increased quantum yield: the former is unity at infinite thione concentration. It was at first

(59) In this it differs from the parallel oxetane formation from acetone, propionaldehyde, and cyclohexanone with the same substrate. These give a mixture of products not simply determined by the energy differences of the radical intermediates: S. H. Schroeter and C. M. Orlando, *J. Org. Chem.*, **34**, 1181 (1969); N. J. Turro and P. A. Wriede, *J. Am. Chem. Soc.*, **92**, 320 (1970). The reaction with acrylonitrile also differs in regiospecificity from that observed with acetone. In the latter case the reaction has been shown to pass via the ketone singlet and an exciplex and not through a triplet biradical: J. A. Barltrop and H. A. J. Carless, *J. Am. Chem. Soc.*, **94**, 1951 (1972).
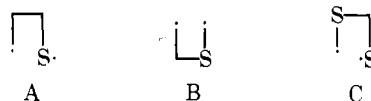
(60) V. Ramamurthy and A. Lawrence, unpublished observations.

(61) D. R. Dice and R. P. Steer, *J. Am. Chem. Soc.*, **96**, 7361 (1974); D. R. Dice and R. P. Steer, *J. Chem. Soc., Chem. Commun.*, **106** (1973); see, however, M. C. Caserio, W. Lauer, and T. Novinson, *J. Am. Chem. Soc.*, **92**, 6082 (1970), for a contrary observation. I thank Professor Steer (University of Saskatchewan) for helpful comments and additional information.

Scheme XI
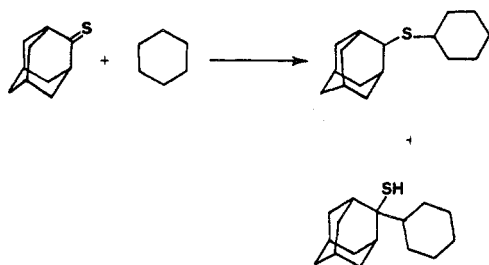
thought that this increased yield was due to a greater population of T_1 via T_n.[62] This was not the case, and the reactivity of the two states is clearly distinguishable. As appears to be the case with aromatic thiones, the S_2 state of adamantanethione is not regiospecific in its addition to electron-rich or electron-deficient olefins, unlike the T_1 state. Furthermore, its addition to fumaronitrile is stereospecific, again in contrast to the T_1 state.[63]

There are other differences between the chemistry of the S_2 and T_1 states. The former is able to react with the hydrocarbon solvent, the products being those of insertion in both senses[63] (see Scheme XI). No indication of the presence of radical intermediates has yet been found, suggesting a concerted $(2\pi + 2\sigma)$ reaction or a very rapid combination within a solvent cage similar to the aralkyl thione cyclizations. Differential quenching of dimerization and insertion by olefins has established the presence of an excimer.[63]

The apparent insertion into a C–H bond has been observed intramolecularly also. In bridged systems (Scheme XII), excitation of a thiocarbonyl function adjacent to the bridgehead leads to the formation of cyclopropyl thiols.[64] The reaction differs from the β-insertion process in the aralkyl thione where flexibility permits the movement of the β-CH bond into the thiocarbonyl plane.[65]

The only hydrogen-abstraction process that has been studied involving a lower excited state is that of the reduction of adamantanethione by the corresponding thiol.[67] The reaction is clean and leads to the formation of the disulfide. The quantum yield is

Scheme XII
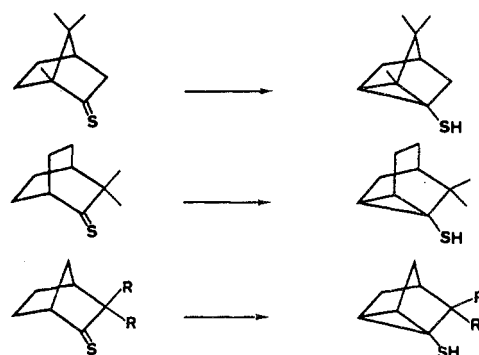
R=Me, Et, Pr or Bu

high ($\sim$1–4), which requires a chain reaction. The use of thiol, deuterated on the carbon α to the sulfur, gave disulfide containing close to one deuterium per molecule, and a chain length of 100 or more was thus indicated. A mechanism equivalent to that illustrated for thiobenzophenone (eq 3) is compatible with these requirements, and support for this was obtained by spin-trapping. In the presence of 2-nitroso-2-methyl-propane ESR signals were obtained consistent with those expected for 11.

11

No signs of reactivity with the hydrocarbon solvent (cyclohexane) were observed following S_1 excitation, in contrast with behavior following S_2 excitation.

Conclusion

The foregoing indicates that thiones may react from upper as well as lower states. In those reactions proceeding via T_1, cycloadditions are nonstereospecific and appear to be more regiospecific than their ketonic counterparts. Complications may ensue by the trapping of intermediates by ground-state thione.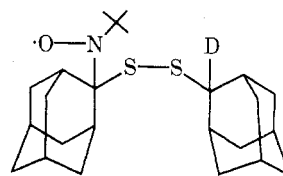 In addition, the triplets are quenched by ground-state thione, possibly by frustrated 1,3- (or 1,2-) dithietane formation, or via decay of a triplet excimer, or both. Hydrogen abstraction requires that the C–H bond be weakened by substitution.

Reaction from S_2—an area of solution photochemistry so far for simple chromophores the private property of the thione[6]—leads to formal insertion into a C–H bond without activation, both inter- and intramolecularly. The insertion appears to be non-regiospecific if the steric situation permits it, interaction being with the π,π^* volume of space, rather than the nonbonding p lobe, as in the former situation. Addition to the olefinic linkage appears to be non-regiospecific, but stereospecific. In these senses S_2 behavior appears carbene-like. There is kinetic evidence for complexes in certain of the cycloadditive reactions supported in the thiobenzophenone–acrylonitrile system by the isolation of a termolecular adduct.

The practical application of thione photochemistry to synthesis is presently limited by the necessity for

(62) See A. Lawrence and P. de Mayo, *J. Am. Chem. Soc.*, **95**, 4084 (1973). The explicit assumption was made there that the paths via S_2 or S_1 both passed through T_1 as the active intermediate. We misled ourselves in that (a) $k_q\tau$ for the quenching of triplet and of adduct (at S_2) were the same (b) dimer was formed in both cases and (c) we failed to detect the thietane stereoisomer (identical retention time on GLC) immediately.

(63) A. H. Lawrence, Ph.D. Thesis, University of Western Ontario, 1974; V. Ramamurthy, unpublished observations.

(64) D. S. L. Blackwell and P. de Mayo, *J. Chem. Soc., Chem. Commun.*, 130 (1973); D. S. L. Blackwell, unpublished observations.

(65) Abstraction of a β-hydrogen and cyclopropanol formation has been recorded, apparently, only once [P. Gull, H. Wehrli, and O. Jeger, *Helv. Chim. Acta*, **54**, 2158 (1971)], and may in that instance proceed by sequential (non-β) hydrogen transfers. The occurrence of β-hydrogen abstraction by nonaromatic ketones, but with the formation of other products than cyclopropanols, has occasionally been reported (see, for example, ref 66). In all these cases hydrogen abstraction and biradical formation are clearly indicated. A similar process has been suggested for the photoenolization of α-diketones: J. Lemaire, *J. Phys. Chem.*, **71**, 2653 (1967); R. Bishop and N. K. Hamer, *J. Chem. Soc. C*, 1197 (1970).

(66) R. A. Cormier, W. L. Schreiber, and W. C. Agosta, *J. Chem. Soc., Chem. Commun.*, 729 (1972); J. R. Scheffer, J. Trotter, R. Wostradowski, C. S. Gibbons, and K. S. Bhandari, *J. Am. Chem. Soc.*, **93**, 3813 (1971); J. R. Scheffer, K. S. Bhandari, R. E. Gayler, and R. H. Wiekenkamp, *ibid.*, **94**, 285 (1972); J. R. Scheffer, K. S. Bhandari, R. E. Gayler, and R. H. Wostradowski, *ibid.*, **97**, 2178 (1975).

(67) J. R. Bolton, K. S. Chen, A. H. Lawrence, and P. de Mayo, *J. Am. Chem. Soc.*, **97**, 1832 (1975).

blocking groups to restrain ground-state reactivity. Should methods be found to circumvent this, a number of useful procedures would become available.

Use of Lithium Organocuprate Additions as Models for an Electron-Transfer Process

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The addition of nucleophiles, $N:^-$, to unsaturated carbonyl compounds, 1 (or other electrophiles), can occur either by direct nucleophilic addition to form the product 4 or as a two-stage reaction in which only an electron is transferred from $N:^-$ to 1 in the first stage. Subsequent coupling of radical intermediates 2 and 3 to form 4 constitutes the second stage of this latter process. A distinction between these mechanistic possibilities has several practical consequences.

In the two-stage pathway, the equilibrium position for the first step, the reversible transfer of an electron, can be estimated from the electrode potential, E_{ox}, for oxidation (loss of an electron) of the nucleophile, $N:^-$, and the corresponding potential, E_{red}, for reduction (gain of an electron) of the carbonyl compound 1. The electrode potentials, E_{ox} and E_{red}, used in this Account refer to the potential, measured by standard polarographic or cyclic voltammetry techniques in an aprotic solvent (usually dimethylformamide) with respect to a saturated calomel electrode, associated with the following reaction: oxidized reactant + $e^- \rightleftarrows$ reduced reactant. With this sign convention, the most powerful reducing agents, $N:^-$, have the most negative E_{ox} values and the most difficultly reduced unsaturated carbonyl compounds 1 have the most negative E_{red} values. Thus, when the value $E_{red} - E_{ox}$ is positive, transfer of an electron from $N:^-$ to the carbonyl compound 1 is energetically favorable.

To obtain sufficient concentrations of intermediates 2 and 3 (ca. 10^{-3} M or greater) so that the second coupling reaction, 2 + 3 → 4, can occur at a reasonable rate, the electrode potential difference, $E_{red} - E_{ox}$, should be more positive than −0.4 V. Consequently, any reaction that proceeds only by the two-stage process would be expected to fail (or to proceed very slowly) if structural changes in $N:^-$ and/or the enone 1 cause the potential difference $E_{red} - E_{ox}$ to become more negative than −0.4 V.

For reactions that can occur by either pathway, the mechanism would be expected to change with structural changes in the reactants that cause the value, $E_{red} - E_{ox}$, to change from values more negative than ca. −0.4 V to more positive values. Of particular importance is the possibility that this change in mechanism may be accompanied by a change in product structure since the charge densities in the original reactants 1 and $N:^-$ and the spin densities in the radical intermediates 2 and 3 may differ. Thus, the locations of highest spin density in the intermediates 2 and 3 could be useful in predicting the structure of the major product formed by a two-stage reaction.

Finally, in any two-stage reaction where the rate of electron transfer is comparable to or more rapid than the subsequent coupling of intermediates 2 and 3, the lifetime of these intermediates may be sufficient to allow other reactions to intervene. For example, one or both of these intermediates 2 or 3 might dimerize or might undergo a stereochemical or structural rearrangement prior to coupling.

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