J. Org. Chem. 1984, 49, 3069–3083 3069

90762-95-1; **17**, 90762-96-2; **18** (α-isomer), 90762-97-3; **18** (β-isomer), 90762-98-4; **19** (α-isomer), 90762-99-5; **19** (β-isomer), 90763-00-1; **20**, 34296-99-6; **21**, 90763-01-2; **22**, 90763-02-3; **23**, 90763-03-4; **24**, 90763-04-5; **25**, 90763-05-6; **26**, 78138-31-5; **27**, 90763-06-7; **28**, 90763-07-8; **29**, 90763-08-9; **30**, 90763-09-0; **31** (α-isomer), 90763-10-3; **31** (β-isomer), 90790-04-8; 3,4-di-*o*-acetyl-1,5-anhydro-2,6-dibromo-2,6-dideoxy-D-*arabino*-hex-1-enitol, 90763-11-4.

Reactivity of Aryl Vinyl Di-π-methane Systems. Mechanistic and Exploratory Organic Photochemistry[1,2]

Howard E. Zimmerman* and Richard L. Swafford

Chemistry Department, University of Wisconsin, Madison, Wisconsin 53706

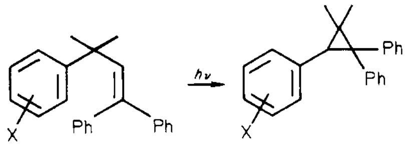
Received December 20, 1983

The di-π-methane rearrangement of a series of meta and para substituted arylvinylmethane reactants was investigated with the aim of determining the patterns of reactivity in systems in which initial excitation is localized in the aryl moiety. Thus the photochemistry of 3-methyl-3-phenyl-1-butene, 3-methyl-3-(*p*-cyanophenyl)-1-butene, 3-methyl-3-(*m*-cyanophenyl)-1-butene, 3-methyl-3-(*p*-methoxyphenyl)-1-butene, and 3-methyl-3-(*m*-methoxyphenyl)-1-butene was studied. The five systems rearranged photochemically to afford corresponding 1,1-dimethyl-2-arylcyclopropanes. The photochemistry of the cyclopropanes was also studied. Each of these opened to the corresponding 1,3-diradical, which then partitioned itself to isomeric 1-aryl-3-methylbutenes. The two processes observed were a 1,4-hydrogen transfer in the diradical and a 1,2-hydrogen shift. Di-π-methane quantum yields were determined. Also, biacetyl studies permitted determination of singlet vs. triplet reactivity. In the di-π-methane rearrangements it was determined that, on direct irradiation, the parent arylvinylmethane and the (cyanophenyl)vinylmethanes reacted only via the singlet excited states, while the anisyl di-π-methane reactants utilized both the singlet and the triplet for rearrangement. However, acetone sensitization was successful in generating the (cyanophenyl)vinylmethane triplets which then rearranged successfully. The main impediment to triplet di-π-methane rearrangement of the cyanoaryl reactants proved to be relatively inefficient intersystem crossing. In the case of the *m*-methoxyphenyl reactant it was possible to determine the triplet lifetime. Finally, singlet rates of decay and reaction were determined for the di-π-methane systems.

Introduction

Quite some years ago we noted that photochemical reactants having two π chromophores bonded to an sp^3 hybridized carbon undergo a general reaction; we termed this the di-π-methane rearrangement.[3] The initial example which precipitated our recognition of the reaction was the barrelene to semibullvalene conversion.[3d,e] Since that time, the reaction has proven itself to be one of the most general of photochemical reactions. Thus, we felt it was deserving of detailed further investigation.

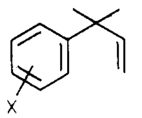
One system of importance consisted of the aryl(diphenylvinyl)methanes **1** which afforded a series of vinylcyclopropanes **2**[3g,3l] by way of the first excited singlet states. Note eq 1. In these reactants the electronic excitation was shown to be heavily localized in the diphenylvinyl chromophore. It seemed to be of particular interest to investigate the behavior of a related set of di-π-methane reactants in which the initial excitation is concentrated in the aromatic ring. Thus the arylvinylmethanes **3**–**5**, bearing meta and para cyano and methoxyl groups, were investigated.



(1)

1 **2**

X = H, *p*-Br, *p*-MeO, *m*-MeO, *p*-CN



3, X = H
4a, X = *p*-MeO
4b, X = *m*-MeO
5a, X = *p*-CN
5b, X = *m*-CN

Results

Synthesis of Photochemical Reactants and Potential Photoproducts. The previously unknown di-π-

---

(1) This is paper 140 of our photochemical series.

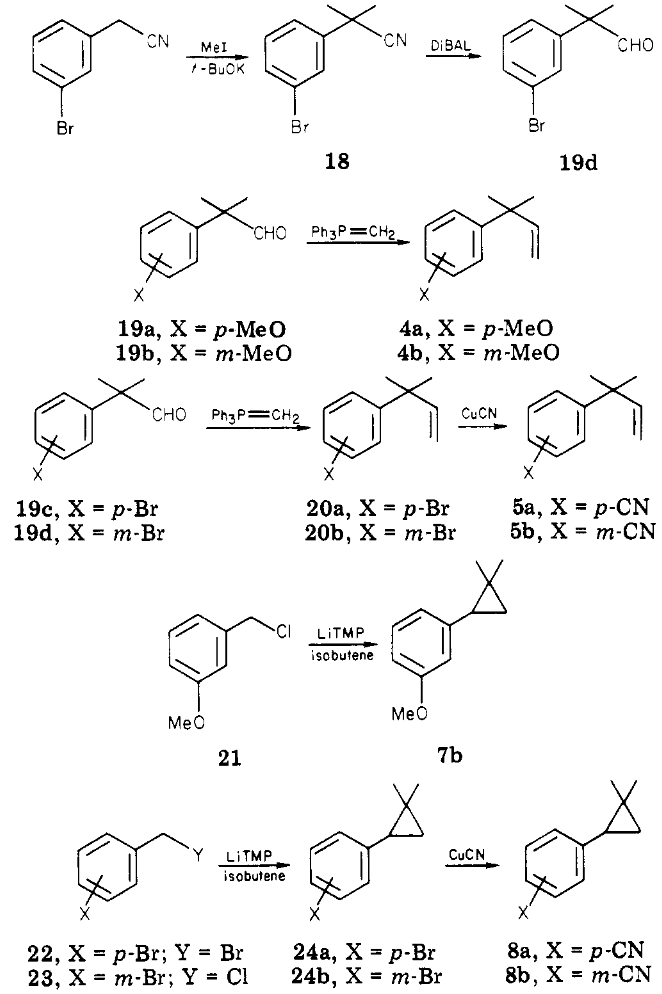
(2) For paper 139, see Zimmerman, H. E.; Wu, G.-S. *Can. J. Chem.* **1983**, *61*, 866–872.

(3) (a) Zimmerman, H. E.; Binkley, R. W.; Givens, R. S.; Sherwin, M. A. *J. Am. Chem. Soc.* **1967**, *89*, 3932–3933. (b) Zimmerman, H. E.; Mariano, P. S. *Ibid.* **1969**, *91*, 1718–1727. (c) Zimmerman, H. E.; Pagni, R. *Ibid.* **1968**, *90*, 6096–6108. (d) Zimmerman, H. E.; Grunewald, G. L. *Ibid.* **1966**, *88*, 183–184. (e) Zimmerman, H. E.; Binkley, R. W.; Givens, R. S.; Grunewald, G. L.; Sherwin, M. A. *Ibid.* **1969**, *91*, 3316–3323. (f) Zimmerman, H. E.; Welter, T. R. *Ibid.* **1978**, *100*, 4131–4145. (g) Zimmerman, H. E.; Steinmetz, M. G.; Kreil, C. L. *Ibid.* **1978**, *100*, 4146–4162. (h) Zimmerman, H. E.; Blinn, J. R. *Tetrahedron* **1981**, *19*, 3237–3243. (i) Zimmerman, H. E.; Wu, G-S. *Can. J. Chem.* **1983**, *61*, 866–871. (j) For a general review see: Hixson, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531–551. Also see ref 3k. (k) Zimmerman, H. E. In "Rearrangements in Ground and Excited States"; DeMayo, P., Ed.; Academic Press: New York, 1980; Vol. 3. (l) A series of styryl para substituted arylmethanes was studied by Hixson.[4]

(4) Hixson, S. S. *J. Am. Chem. Soc.* **1972**, *94*, 2507–2508.

0022-3263/84/1949-3069$01.50/0 © 1984 American Chemical Society

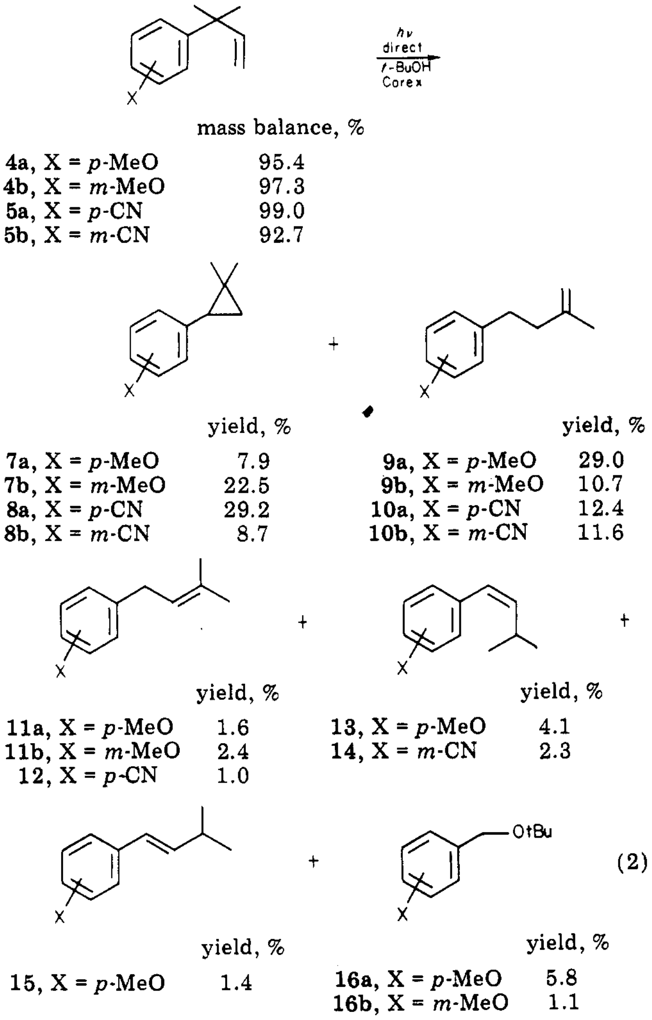
Scheme I. Synthesis of Di-π-methane Reactants and Potential Photoproducts



methane reactants 4–5 were prepared as outlined in Scheme I. Also, as the study developed, it was apparent that a number of secondary photoproducts would require structure elucidation. These were independently synthesized as depicted in Scheme II.

Exploratory Photochemistry. Direct Irradiation of Di-π-methane Reactants. Previously[5] the photochemistry of 3-methyl-3-phenyl-1-butene (3) has been observed to afford 1,1-dimethyl-2-phenylcyclopropane (6) on direct irradiation. In the present study reactants 4a, 4b, 5a, and 5b were observed to undergo a facile reaction under preparative conditions, affording the corresponding arylcyclopropanes 7a, 7b, 8a, and 8b. The reaction is shown in eq 2. It is seen that, in addition to the di-π-methane rearrangement products, a series of aryl substituted butenes was encountered. In the case of *p*-methoxy and *m*-methoxy reactants, there were observed the corresponding *tert*-butyl aryl ethers. The product distribution under preparative conditions is included in eq 2. We note, however, that only the arylcyclopropanes are primary photoproducts (vide infra).

Exploratory Photochemistry. Secondary Reactions. Direct irradiation of the arylcyclopropanes led to three types of products with the distribution depending on reactant substitution. The aryl 1-butenes 9 and 10 derive from three-membered ring opening and 1,4-hydrogen transfer. The aryl-2-butenes 11 and 12 as well as styryl derivatives 13, 14, and 15 derive from a different mechanism as discussed below. The *tert*-butyl ethers 16 arise from carbene fragmentation (vide infra). The secondary reactions are summarized in eq 3.



	mass balance, %
4a, X = *p*-MeO	95.4
4b, X = *m*-MeO	97.3
5a, X = *p*-CN	99.0
5b, X = *m*-CN	92.7

	yield, %
7a, X = *p*-MeO	7.9
7b, X = *m*-MeO	22.5
8a, X = *p*-CN	29.2
8b, X = *m*-CN	8.7

	yield, %
9a, X = *p*-MeO	29.0
9b, X = *m*-MeO	10.7
10a, X = *p*-CN	12.4
10b, X = *m*-CN	11.6

	yield, %
11a, X = *p*-MeO	1.6
11b, X = *m*-MeO	2.4
12, X = *p*-CN	1.0

	yield, %
13, X = *p*-MeO	4.1
14, X = *m*-CN	2.3

	yield, %
15, X = *p*-MeO	1.4

	yield, %
16a, X = *p*-MeO	5.8
16b, X = *m*-MeO	1.1

(2)

Exploratory Photochemistry. Sensitized Irradiations of the Di-π-methane Reactants. Of the three types of systems—unsubstituted, methoxy bearing, and cyano substituted—only the last had a triplet energy (i.e., 77 kcal/mol[6]) sufficiently below that of useful sensitizers as acetone (E_T 80 kcal/mol[7]) to permit reasonably efficient sensitization; note eq 4. The reaction was noteworthy in lacking the secondary photoproducts characteristic of the direct irradiation runs, and this is of synthetic significance (note below).

Quantum Yield and Singlet Rate Studies. Direct quantum yields (i.e. ϕ_{dir}) for all compounds and the sensitized quantum yields for the cyano derivatives 5a and 5b were determined. These are summarized in Table I. These efficiencies of course include, at least potentially, both singlet and triplet contributions. One noteworthy point is the very wide range of the quantum efficiencies in the direct irradiations, ranging from 0.0058 in the case of the parent phenyl butene 3 to the 0.18 value for the *p*-cyano butene 5a. Equally remarkable, an efficiency of 0.71 was observed for the sensitized efficiency of the *p*-cyano butene 5a. There appears to be no literature describing triplet efficiencies of di-π-methane rearrangements of this type of simple arylvinylmethane.

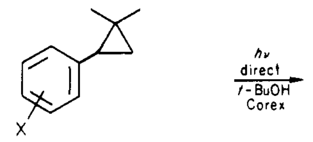
It was important to determine the singlet lifetimes of the reactants. These are necessary in determining rates

---

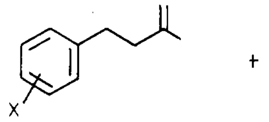
(5) Fasel, J. P.; Hansen, H. J. *Chimia* **1981**, *35*, 9–12.

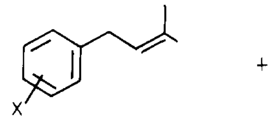
(6) Lewis, G. N.; Kasha, M. *J. Am. Chem. Soc.* **1944**, *66*, 2100–2116.

(7) Borkman, R. F.; Kerns, D. R. *J. Chem. Phys.* **1966**, *44*, 945–949.



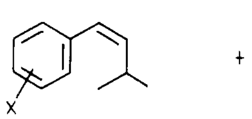
	mass balance, %
7a, X = *p*-MeO	95.1
7b, X = *m*-MeO	96.1
8a, X = *p*-CN	99.4
8b, X = *m*-CN	95.0

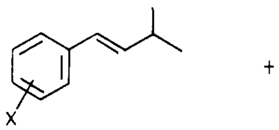




	yield, %
9a, X = *p*-MeO	38.2
9b, X = *m*-MeO	26.8
10a, X = *p*-CN	30.1
10b, X = *m*-CN	28.8

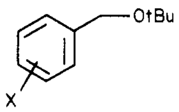
	yield, %
11a, X = *p*-MeO	2.5
11b, X = *m*-MeO	10.0
12, X = *p*-CN	2.5





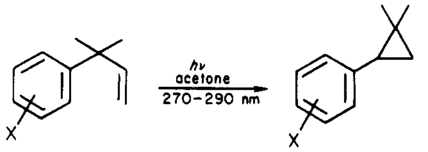
	yield, %
13, X = *p*-MeO	6.7
14, X = *m*-CN	8.9

	yield, %
15, X = *p*-MeO	2.5



(3)

	yield, %
16a, X = *p*-MeO	12.7
16b, X = *m*-MeO	2.9



(4)

	mass balance, %
8a, X = *p*-CN	97.5
8b, X = *m*-CN	97.8

	yield, %
10a, X = *p*-CN	55.3
10b, X = *m*-CN	47.5

of S_1 radiationless decay and also singlet reaction rates.[8] The singlet lifetimes (i.e, the inverse of the total rate of singlet decay) are of intrinsic interest. The method of single photon counting[8,9] as described by us previously[8] was employed. In our more recent studies we have used an on-line PDP-11 rather than the original PDP-8. The method uses the minicomputer as a multichannel analyzer and also for data reduction. Most useful is the algorithm we devised[8] which gives a stable least-squares fit to the observed decay curve, taking into account, by deconvolution, the effect of the lamp flash function. In this method both preexponential and exponential terms are varied in a decay function taken as a sum of exponentials. The lifetimes and rates of decay obtained are summarized in Table II.

Singlet Reaction Rates. In our previous efforts we have used singlet lifetimes (i.e., $^1\tau$), or alternatively, total rates of singlet decay (i.e., $^1k_{dtot}$), along with singlet reaction

Scheme II. Synthesis of Potential Secondary Photoproducts

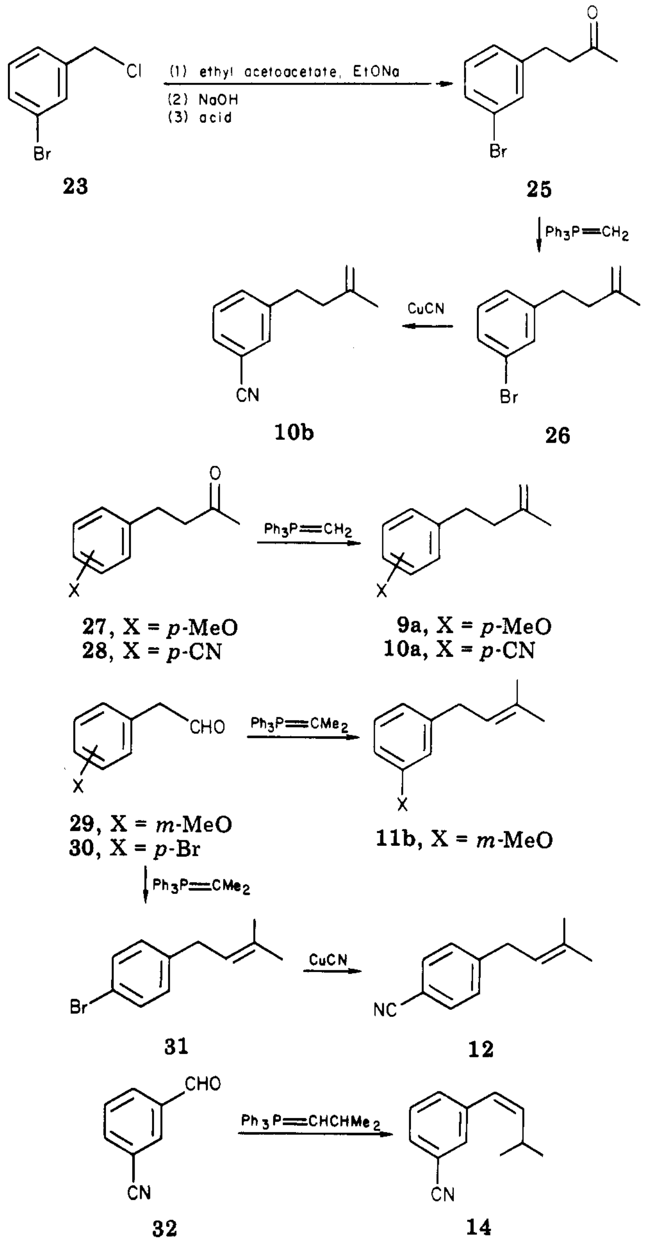


Table I. Summary of Quantum Yield Determinations

arylbutene reactant	sensitizer	cyclopropane photoproduct	quantum yield
phenylbutene (**3**)	none	**6**	0.0058
(*p*-methoxyphenyl)butene (**4a**)	none	**7a**	0.051
(*m*-methoxyphenyl)butene (**4b**)	none	**7b**	0.059
(*p*-cyanophenyl)butene (**5a**)	none	**8a**	0.18
(*p*-cyanophenyl)butene (**5a**)	acetone	**8a**	0.71
(*m*-cyanophenyl)butene (**5b**)	none	**8b**	0.064
(*m*-cyanophenyl)butene (**5b**)	acetone	**8b**	0.25

Table II. Single Photon Counting Results

reactant	$^1\tau$, ns	$^1k_{dtot}$, s^{-1}	^1k_r, s^{-1}
phenylbutene (**3**)	9.2	1.1×10^8	6.4×10^5
(*p*-methoxyphenyl)butene (**4a**)	4.4	2.3×10^8	1.0×10^7
(*m*-methoxyphenyl)butene (**4b**)	4.6	2.2×10^8	7.7×10^6
(*p*-cyanophenyl)butene (**5a**)	10.3	9.7×10^7	1.8×10^7
(*m*-cyanophenyl)butene (**5b**)	4.9	2.0×10^8	1.3×10^7

---

(8) (a) Zimmerman, H. E.; Werthemann, D. P.; Kamm, K. S. *J. Am. Chem. Soc.* **1973**, *95*, 5904–5905. (b) Zimmerman, H. E.; Werthemann, D. P.; Kamm, K. S. *Ibid.* **1974**, *96*, 439–449.

(9) Bollinger, L. M.; Thomas, G. E. *Rev. Sci. Instrum.* **1961**, *32*, 1044–1050.

Table III. Triplet Parameters

reactant	$^3\tau$, ns	$[P/F]_{270}/[P/F]_{420}$[a]	k_{isc}, s^{-1}
phenylbutene (**3**)	no triplet[b]	0.994	
(*p*-methoxyphenyl)butene (**4a**)	*c*	*d*	
(*m*-methoxyphenyl)butene (**4b**)	175	*d*	9.2×10^6
(*p*-cyanophenyl)butene (**5a**)	no triplet[b]	1.023	
(*m*-cyanophenyl)butene (**5b**)	no triplet[b]	1.009	

[a] *P/F* at λ where reactant absorbs is normalized by *P/F* where biacetyl alone absorbs. [b] No triplet detected on direct irradiation. [c] Triplet detected but reliable lifetime not obtainable. [d] Biacetyl concentration dependent.

quantum yields (i.e., $^1\phi_r$) to obtain rates of excited singlet reactions.[8,10] See eq 5. We note that the required singlet

$$^1k_r = {^1\phi_r}/{^1\tau} = {^1k_{dtot}}{^1\phi_r} \qquad (5)$$

reaction quantum yield constitutes at most a portion of the direct efficiency. The dissection of $^1\phi_r$ from the ϕ_{dir} obtained experimentally is described in the section below on biacetyl studies. In contrast to $^1k_{dtot}$, which corresponds to a directly observable process, ^1k_r needs definition. Thus ^1k_r is equal to the rate of disappearance of the excited singlet by all processes multiplied by the probability of S_1 reacting rather than undergoing radiationless decay, fluorescing, intersystem crossing, etc. Hence ^1k_r is an operational rate constant corresponding to the effective rate of S_1 leading to product. These reaction rates are included in Table II.

Biacetyl Studies. Triplet Interception and Quenching. Biacetyl has been of special value for excited-state quenching[10,11] because of its room temperature fluorescence and phosphorescence which provides a direct indication of whether energy transfer is from a singlet or a triplet donor. One way to determine the extent of interception of triplets by biacetyl is to monitor the phosphorescence relative to the fluorescence intensity, that is, the emission at 510 and 460 nm, respectively. The characteristic ratio of phosphorescence to fluorescence—originating from biacetyl singlet which intersystem crosses and phosphoresces in competition with its fluorescence—is in the range of 8.7:1[12] to 16.5:1.[10d] To the extent that a singlet is intercepted by biacetyl, this ratio remains the same as if biacetyl had absorbed light itself, since events begin with S_1 of biacetyl. However, as triplets are intercepted, biacetyl phosphorescence is enhanced relative to the fluorescence.

In three of the five molecular systems studied—the parent phenylbutene **3** and the two (cyanophenyl)butenes **5a** and **5b**—biacetyl interception of excited states showed essentially no phosphorescence enhancement. Five percent proceeding via the triplet would have been readily detected as long as the triplet lifetimes were of the order of ca. 20 ns. Hence it could be assumed that no triplet was formed in the direct irradiation (note Table III). Thus in these instances the direct quantum yields could be taken to be singlet quantum yields.

Biacetyl Studies. Quantitative Dissection of Singlet and Triplet Reaction Components. For the remaining two compounds, the anisylbutenes **4a** and **4b**, a quantitative dissection of observed direct quantum yields into singlet and triplet components was desired.

Table IV. Summary of Quenched Quantum Yield Determinations

arylbutene reactant	biacetyl concn, M	cyclopropane photoproduct	quantum yield
(*p*-methoxyphenyl)butene (**4a**)	0.0030	**7a**	0.0375
(*m*-methoxyphenyl)butene (**4b**)	0.00084	**7b**	0.0405

Table V. Singlet and Triplet Efficiencies for (Methoxyphenyl)butenes 4

arylbutene reactant	$^1\phi_r$	$\phi_{isc}\,{^3\phi_r}$	$^3\phi_r$
(*p*-methoxyphenyl)butene (**4a**)	0.044	0.0067	
(*m*-methoxyphenyl)butene (**4b**)	0.0354	0.0239	0.563

For this dissection the efficiency of intersystem crossing and the triplet lifetime were first needed. The method of Sandros[10e] proved useful. The function *S* of eq 6 is plotted

$$S = [(P/F)_{270}(P/F)_{420}{}^{-1} - 1]^{-1} = ({^1k_q}/k_{isc,x})[\mathrm{Bi}] + ({^1k_q}{^3k_{dtot,x}}/{^3k_q}k_{isc,x}) \qquad (6)$$

against biacetyl concentration. Here *P* and *F* represent phosphorescence and fluorescence intensities, respectively; the excitation wavelength is given as a subscript. X refers to an added compound able to transfer excitation to biacetyl. A plot of *S* vs. biacetyl concentration (i.e., [Bi]) should be linear and affords from the slope and intercept the rate of intersystem crossing of the unknown X and also the total rate of triplet decay (i.e., the inverse of the triplet lifetime).

For the *m*-methoxy butene **4b** a linear plot was obtained and afforded the results included in Table III. In addition, for the *m*-methoxy butene **4b** we can derive the efficiency of intersystem crossing, since $k_{isc} = {^1k_{dtot}}{^1\phi_{isc}}$. For three of the remaining arylbutenes—**3**, **5a**, and **5b**—over a range of biacetyl concentrations, the phosphorescence was not enhanced within experimental error and inspection of the function *S* revealed the $(P/F)_{270}(P/F)_{420}{}^{-1}$ portion to be unity within experimental error, leading *S* to be measured as infinite. This suggests that the rate of singlet energy transfer is exceedingly large compared with the rate of intersystem crossing of compound X under study. For the *p*-methoxy butene **4a**, this situation was approached sufficiently that a reproducible plot could not be obtained. Fortunately, for this case the intersystem crossing efficiency and triplet decay rate proved unnecessary (vide infra).

Also required for the dissection of direct irradiation efficiency of **4a** and **4b** into singlet and triplet processes was the reaction quantum yield under conditions where the arylbutene triplets were being quenched. The small span between the singlet and triplet lifetimes led to singlet quenching under conditions necessary to quench triplets. Table IV provides sample quenched quantum yields for the methoxy butenes **4a** and **4b** at useful biacetyl concentrations.

The data now available included the rates of intersystem crossing, the rates of triplet decay, the direct quantum yields, the singlet lifetimes, and the quenched quantum yields. With this information in hand, the dissection was possible. Thus, a direct quantum yield is given as in eq 7. Substitution of quantum yield definitions leads to eq

$$\phi_{rq}{}^{\mathrm{DIR}} = {^1k_r}/({^1k_{dtot}} + {^1k_q}[\mathrm{Q}]) + [{^1k_{isc}}/({^1k_{dtot}} + {^1k_q}[\mathrm{Q}])({^3k_r}/({^3k_{dtot}} + {^3k_q}[\mathrm{Q}]))] \qquad (7)$$

$$\phi_{rq}{}^{\mathrm{DIR}} = {^1\phi_r}/(1 + {^1k_q}{^1\tau}[\mathrm{Q}]) + [{^1\phi_{isc}}/(1 + {^1k_q}{^1\tau}[\mathrm{Q}])({^3\phi_r}/(1 + {^3k_q}{^3\tau}[\mathrm{Q}]))] \qquad (8)$$

---

(10) (a) Baeckstrom, H. L. J.; Sandros, K. *Acta Chem. Scand.* **1958**, *12*, 823. (b) Dubois, J. T.; Van Hemert, R. L. *J. Chem. Phys.* **1964**, *40*, 923–925. (c) Wilkinson, F.; Dubois, J. T. *Ibid.* **1963**, *39*, 377–383. (d) Dubois, J. T.; Wilkinson, F. *Ibid.* **1963**, *38*, 2541–2547. (e) Sandros, K. *Acta Chem. Scand.* **1969**, *23*, 2815–2829.

(11) (a) Zimmerman, H. E.; Kamm, K. S.; Werthemann, D. P. *J. Am. Chem. Soc.* **1974**, *96*, 7821–7823. (b) Zimmerman, H. E.; Kamm, K. S.; Werthemann, D. P. *Ibid.* **1975**, *97*, 3718–3725.

(12) Zimmerman, H. E.; Durr, H. G.; Givens, R. S.; Lewis, R. G. *J. Am. Chem. Soc.* **1967**, *89*, 1863–1874.

Table VI. Calculated Singlet Quantum Yields and Triplet Intervention for the (*p*-Methoxyphenyl)butene (4a)

$^3\tau$, ns	$^1\phi_r$	$\phi_{isc}\,^3\phi_r$
10.0	0.032	0.019
175.0	0.044	0.0067
infinite	0.045	0.0059

8 which takes the available data and provides the singlet efficiency in a direct irradiation. With the singlet reaction efficiency and the intersystem crossing efficiency available, we can subtract out the singlet contribution and obtain the triplet component of the direct quantum yield. The dissected values for the *m*-anisylbutene **4b** are given in Table V.

In the case of the *p*-anisylbutene **4a**, the Sandros plot was not sufficiently reproducible (vide supra) to obtain a triplet lifetime. However, the singlet quantum yield in eq 8 proved remarkably insensitive to the triplet lifetime. This is shown in Table VI where the calculated singlet quantum yields (i.e., the $^1\phi_r$'s) are given for a range of assumed $^3\tau$ values as long as this triplet lifetime is ca. 10 ns or above. With a lifetime of 175 ns for the meta isomer **4b**, this assumption seems reasonable and leads to a value of $^1\phi_r = 0.044$ for the singlet quantum yield with an uncertainty of 15%.

With the singlet contribution $^1\phi_r$ for the reaction of the *p*-methoxy butene **4a** known, one can subtract this from the total reaction quantum yield to obtain the effective triplet contribution. However, this is the product $(\phi_{isc})(^3\phi_r)$ and, in principle, not susceptible to the dissection. We do note that the singlet lifetimes for the *p*- and *m*-methoxy butenes **4a** and **4b** are similar as are the singlet efficiencies (note above in Tables II and V), thus suggesting that ϕ_{isc} is relatively independent of *m*- vs. *p*-methoxy substitution. With ϕ_{isc} being taken as ca. 0.043 as observed for the meta isomer, we obtain $^3\phi_r = 0.16$.

For the single case of the (*m*-methoxyphenyl)butene **4b** the rate of triplet rearrangement could be obtained from eq 9, since the required rate of triplet decay and triplet quantum yields were available. ^3k_r was found to be 3.2×10^6 s^{-1}.

$$^3k_r = {^3\phi_r}\,{^3k_{dtot}} \qquad (9)$$

Thus biacetyl methods often prove quite useful in dissection of singlet and triplet components.

Interpretative Discussion

Multiplicity of the Rearranging Di-π-methane Species. In contrast to our previous aryl vinyl di-π-methane system,[3g] the molecules presently studied revealed both singlet and triplet reactivity. Thus, in the present study quenching by biacetyl showed that the *m*- and *p*-anisylvinylmethanes **4a** and **4b** were, indeed, rearranging partially via the triplet excited state. Also, sensitization of the (*m*- and (*p*-cyanophenyl)vinylmethanes **5a** and **5b** provided evidence for the ability of the triplets of these reactants to rearrange. In addition, although the cyano substituted molecules did not intersystem cross, they did rearrange, thus showing the ability of singlets to rearrange as well as triplets. Parallel to our own results, it has been observed in qualitative studies by Hansen[5,13] that several arylvinylmethanes were capable of reaction on sensitization. These were systems having no or one methyl group on the methane carbon and also unsubstituted vinyl groups.

Table VII. Singlet Quantum Efficiencies

	quantum yield	
arylbutene reactant	$^1\phi_r$	source[a]
phenylbutene (**3**)	0.0058	direct
(*p*-methoxyphenyl)butene (**4a**)	0.044	dissection
(*m*-methoxyphenyl)butene (**4b**)	0.035	dissection
(*p*-cyanophenyl)butene (**5a**)	0.18	direct measurement
(*m*-cyanophenyl)butene (**5b**)	0.064	direct measurement

[a] Whether obtained as the direct irradiation quantum yield or, alternatively, by dissection of the direct efficiency as described in the Result section.

The structural feature which seems responsible for permitting a triplet di-π-methane rearrangement, despite the presence of a vinyl potential free rotor,[3b,11b,14] appears to be lack of phenyl substitution on the vinyl group. This point is discussed below in connection with energy partition in the excited states. However, for the moment, it is seen that the reactive arylvinylmethane triplets may be anticipated to have the aryl group as the low-energy chromophore, while the unreactive triplets have a diphenylvinyl or styryl moiety as the low-energy chromophore.

Although both singlets and triplets of the systems under study are capable of di-π-methane rearrangement, there is a wide spread in intersystem crossing efficiencies so that on direct irradiation the *p*-cyano, *p*-methoxyl, and the parent phenyl systems utilize the triplets to different extents. The parent phenylvinylmethane **3** reacts only via the singlet on direct irradiation, and it is interesting to compare the elegant study by Morrison[15] showing *tert*-butylbenzene to be the least efficient of alkylbenzenes in intersystem crossing ($\phi_{isc} = 0.086$, contrast $\phi_{isc} = 0.52$ for toluene). With less side chain substitution the efficiency increases. The parent di-π-methane reactant **3** is similar to *tert*-butylbenzene in having a bulky side chain.

Similarly, the cyano substituted systems **5a** and **5b** show no intersystem crossing and only singlet reactivity on direct irradiation. In contrast the methoxy derivatives **4a** and **4b** intersystem cross to afford triplets in competition with the singlet rearrangement, and thus give both singlet and triplet reactivity on direct irradiation. The intersystem crossing efficiency for anisole itself is 0.74[16] which contrasts with the 0.043 value for the *m*-methoxy di-π-methane reactant **4b**. It may be that the bulky side chain substitution plays a role here in inhibiting intersystem crossing.

Singlet Reaction Efficiencies. Despite intervention to varying extent by the triplet, we find that all of the systems rearrange smoothly via S_1 (refer to Table VII). Interestingly, the spread of these singlet reaction efficiencies—$\phi = 0.0058$ for the parent phenylbutene **3** to $\phi = 0.18$ for the (*p*-cyanophenyl)butene **5a**—is greater than that encountered in our previous study[3g] of the aryl diphenylvinyl butenes **1a**–**1e**. In this diphenylvinyl series the range of efficiencies was narrow, $\phi = 0.24$ to $\phi = 0.058$.

Hixson's pioneering study[4] of a series of arylstyrylmethanes with an unsubstituted methane carbon provides a similarly small spread of quantum efficiencies—$\phi = 0.005$

---

(13) (a) Koch-Pomeranz, U.; Hansen, H-J.; Schmid, H. *Helv. Chim. Acta* **1975**, *58*, 178–182. (b) Dietliker, K.; Hansen, H-J. *Chimia* **1981**, *35*, 52–53. (c) This work, as well as that in ref 4, cites without experimental detail some selected relative quantum yields.

(14) (a) Zimmerman, H. E.; Pratt, A. C. *J. Am. Chem. Soc.* **1970**, *92*, 1409–1411. (b) Zimmerman, H. E.; Pratt, A. C. *Ibid.* **1970**, *92*, 6267–6271. (c) This was first mentioned without being named in ref 3b to rationalize the lack of reactivity of triplet acyclic di-π-methane reactants as contrasted with singlets.

(15) Schloman, W. W., Jr.; Morrison, H. *J. Am. Chem. Soc.* **1977**, *99*, 3342–3345.

(16) Carroll, F. A.; Quina, F. H. *J. Am. Chem. Soc.* **1972**, *94*, 6246–6247.

Table VIII. Triplet Quantum Efficiencies

arylbutene reactant	quantum yield	
	$^3\phi_r$	source
(p-methoxyphenyl)butene (**4a**)	0.3	dissection
(m-methoxyphenyl)butene (**4b**)	0.56	dissection
(p-cyanophenyl)butene (**5a**)	0.71	sensitization
(m-cyanophenyl)butene (**5b**)	0.25	sensitization

for p-methoxy- to $\phi = 0.0013$ for p-cyano-bearing reactants.

The singlet reaction efficiencies correspond to the probability of S_1 reacting to afford product as opposed to just decaying back to ground-state reactant. It proved possible to obtain the excited singlet reaction and decay rates, and thus the reaction efficiencies are discussed further in connection with these rates.

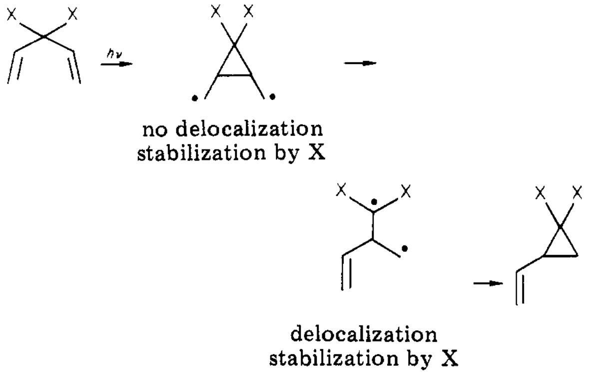
Triplet Reaction Efficiencies. A striking difference was the reactivity of the presently studied aryl vinyl system triplets compared with the diphenylvinyl system studied previously.[3g] As mentioned above (diphenylvinyl)methane systems of our previous study had unreactive triplets. Also, a series of aryl(cyanovinyl)- and aryl(dicyanovinyl)methanes lacking central methyl substitution were shown in a study by Salisbury[17] to have unreactive triplets.

Not only are the triplets of the present study reactive, but in addition, the quantum efficiencies for triplet reactivity are quite high, in the range of 0.25–0.71. Table VIII summarizes these triplet quantum yields.

Although the Hansen study provided[13b] only relative quantum yields, the triplet efficiencies reported are approximately in the same ratio as those we obtained and listed in Table VIII.

Related findings derive from the work of Paquette[18a] and Houk[18b] dealing with the reactivity of aryl substituted benzonorbornadienes and the regioselectivity of bridging. We note that the barrelene variation[3d,3e,19] of the di-π-methane rearrangement proceeds via triplets. The Paquette–Houk study revealed a preference for benzovinyl bridging para to cyano and meta to methoxy on sensitization. This was reminiscent of the meta transmission effect uncovered by us,[20] an effect in which aromatic substituents were shown to interact selectively with meta sites rather than exhibiting the usual ortho–para transmission so characteristic of ground-state chemistry.

Of course the benzobarrelene system is of the type which characteristically reacts preferentially via triplets.[3a,3c–e,19] Of particular interest is the qualitative parallel between the triplet quantum efficiencies presently observed (i.e., Table VIII) and the regioselectivity reported by Paquette[18a] and Houk.[18b] This similarity is particularly intriguing in view of the lack of parallelism demonstrated by the singlet counterparts where the quantum yields of (methoxyphenyl)butenes showed no appreciable difference in efficiency. This is all the more remarkable when one considers that our earlier MO treatment[20] of excited-state meta transmission as well as the subsequent work[18b] are based on one-electron calculations which are multiplicity independent. A further point is that the selectivity reported in the substituted benzobarrelene photochemistry may not be determined in the bridging step of the di-π-methane rearrangement but may result instead from the second step of the di-π-methane mechanism. Note eq 10.



(10)

This is suggested by the dramatic enhancement of triplet reactivity by substitution of delocalizing groups on the methane carbon as in substituted dienes **33**, **34**, and **35**.

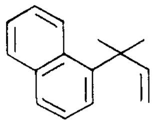
$Ph_2C{=}CHCPh_2CH{=}CMe_2$
33

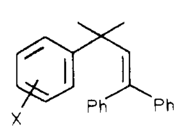
$Ph_2C{=}CHC(CN)_2CH{=}CPh_2$
34

$Ph_2C{=}CHC(COOMe)_2CH{=}CPh_2$
35

Discussion of Singlet Lifetimes. It is interesting to compare the singlet lifetimes of the phenylbutene **3** and anisylbutene **4** reactants both with the lifetimes of the related aromatic compounds as well as with the lifetimes of di-π-methane systems previously studied. Thus, the lifetime of phenylbutene **3** (τ, 9.2 ns, Table II) is only slightly shorter than that of toluene (τ, 35 ns[24]) and virtually the same as that reported[15] for *tert*-butylbenzene (τ, 10 ns). Analogously, the lifetimes of the anisylbutenes **4a** and **4b** (τ, 4.4 and 4.6 ns, Table II) are shorter, but only by a factor of two, than anisole itself (τ, 8.3 ns[24]).

These systems are reminiscent of the naphthylvinylmethane **36** whose singlet lifetime (τ, 63 ns)[3h] was only slightly shorter than that of unreactive alkylnaphthalene counterparts. This situation contrasts with di-π-methane reactants of the type **1** where the lifetimes are exceedingly short and in the range of 19–21 ps or ca. 1000-fold shorter.


36



1

We can ascribe the longer lifetimes of the arylbutenes under study to concentration of electronic excitation energy in the aryl portion of the molecule and not in the free rotor vinyl moiety. This applies equally to the naphthyl system **36** but not the diphenylvinyl systems **1**.

---

[17] (a) In a very pretty study Salisbury and co-workers studied a series of (dicyanovinyl)-[17b] and (cyanovinyl)arylmethanes.[17c] Since all of the examples compared have only monohetero substitution (on the aryl groups), these examples may not be fairly compared quantitatively. (b) Feereiria, A. B. B.; Salisbury, K. *J. Chem. Soc., Perkin Trans. 2* **1978**, 995–1001. (c) Feereiria, A. B. B.; Salisbury, K. *Ibid.* **1982**, 25–29.

[18] (a) Paquette, L. A.; Cottrell, D. M.; Snow, R. A. *J. Am. Chem. Soc.* **1977**, *99*, 3723–3733. (b) Santiago, C.; Houk, K. N. *Ibid.* **1976**, *98*, 3380–3381.

[19] (a) Zimmerman, H. E.; Pagni, R. *J. Am. Chem. Soc.* **1968**, *90*, 6096–6108. (b) Zimmerman, H. E.; Bender, C. O. *Ibid.* **1969**, *91*, 7516–7518. (c) Zimmerman, H. E.; Bender, C. O. *Ibid.* **1970**, *92*, 4366–4376. (d) Zimmerman, H. E.; Viriot-Villaume, M-L. *Ibid.* **1973**, *95*, 1274–1280. (e) Zimmerman, H. E.; Amick, D. R. *Ibid.* **1973**, *95*, 3977–3982.

[20] (a) Zimmerman, H. E.; Sandel, V. R. *J. Am. Chem. Soc.* **1963**, *85*, 915–922. (b) Zimmerman, H. E.; Somasekhara, S. *Ibid.* **1963**, *85*, 922–927.

[21] Zimmerman, H. E.; Boettcher, R. J.; Braig, W. *J. Am. Chem. Soc.* **1973**, *95*, 2155–2163.

[22] Zimmerman, H. E.; Factor, R. E. *Tetrahedron Suppl.* **1981**, *37*, 125–141.

[23] Zimmerman, H. E.; Armesto, D.; Amezua, M. G.; Gannett, T. P.; Johnson, R. P. *J. Am. Chem. Soc.* **1979**, *101*, 6367–6383.

[24] Berlman, I. B. "Handbook of Fluorescent Spectra of Aromatic Molecules"; Academic Press: New York, 1965.

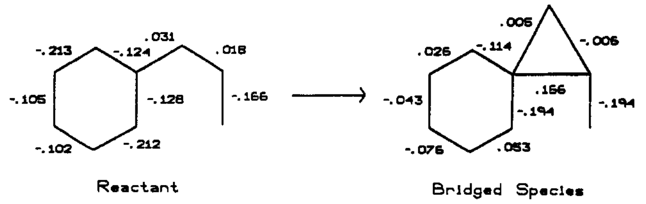


Figure 1. ΔP determination of drift of electronic excitation during bridging in the rearrangement.

Hence we can conclude that utilization of the free rotor effect[3k,11b,14] by an excited state requires appreciable distribution of the excitation energy in the free rotor portion of the molecule. This requirement should apply to both singlets and triplets.

Application of the ΔP and ΔE Method to the Reaction. From the discussion thus far, it is clear that the matter of excitation energy partition is relevant to a variety of phenomena under consideration. Hence it is worthwhile to report the results of application of our ΔP and ΔE method[25] to the aryl vinyl butenes of present interest. The ΔP variation of the method takes the excited-state bond order matrix, giving bond orders between all pairs of orbitals, and subtracts the corresponding ground-state bond order matrix. The matrices used may derive from one-electron calculations, either Hückel or SCF, or instead from SCF–CI treatments. The ΔP matrix then gives the change in all bond orders resulting from the excitation process. Where a ΔP element is negative, the bond order has become more antibonding on excitation and energy is concentrated at that site. Where there is no change, we can conclude that electronic excitation has not perturbed that part of the molecule. In bonds where the ΔP element is positive that part of the molecule is more bonding than in the ground state and energy is drained toward other parts of the molecule. Clearly, there will be more negative than positive ΔP elements.

Thus the ΔP matrix gives a quantitative indication of the distribution of excitation energy. The corresponding ΔE matrix operates in similar fashion but partitions the energy of excitation into bond contributions directly rather than just giving bond orders. Beyond this, one can follow the drift of ΔP's (bond order excitations), or of the ΔE contributions, as an excited state reaction proceeds. Figure 1 depicts the bridging stage of the di-π-methane rearrangement of the arylbutenes under study by using the type of SCF–CI calculations we have previously utilized.[3d]

Most interestingly, in the vertical excited state we find excitation concentrated in the aryl group. This is, as previously qualitatively noted above, in accord with intuition based on the relative energy of the separated chromophores in the molecule, aryl and vinyl. As the di-π-methane rearrangement proceeds in bridging, excitation becomes concentrated in the region of the cyclopropyldicarbinyl moiety. The results are qualitatively, if not semiquantitatively, the same independent of aryl ring substitution. Since excitation is not near the substituent in the bridged species, we can understand the minor effect of substitution in the molecules under study. This point is discussed specifically in the following section.

Discussion of Singlet Reaction Rates. Previously we have mentioned the closely clustered rates of singlet excited-state reactions, except for the relatively slow rate observed for the parent phenylvinylmethane **3**. Thus Table II reveals a small spread in rates, and in our previous study[3g] all of the singlet rates fell within a range of 1:4.5. These rates thus necessarily are reasonably independent of meta vs. para substitution as well as independent or aryl substitution in general. This independence seems to reflect the small difference in effect of the substitution on the energy of the bridged cyclopropyldicarbinyl bridged species due to excitation being concentrated in parts of the molecule other than the aryl group. We might therefore expect control by the energy of the starting vertical singlet excited state. However, except for the parent phenylbutene **3** these compounds have quite similar absorption maxima near 280 nm and thus similar singlet energies. Hence the energy of converting the vertical excited state to the cyclopropyldicarbinyl species will vary very little. The slow rate of the phenyl example is not due to an energetic effect, since its vertical excited state is of higher energy than its companions as a consequence of its absorption at 260–265 nm.

Table IX. C-1 and C-8 LCAO MO Coefficients in HOMO and LUMO of the Cyclopropyldicarbinyl Diradicals

diradical	LCAO MO coefficients			
	C-1		C-8	
	HOMO	LUMO	HOMO	LUMO
parent system **37**	0.6040	0.6010	−0.3255	0.3350
p-methoxy **38**	0.6105	0.5817	−0.2974	0.3385
m-methoxy **39**	0.5956	0.6038	−0.2931	0.3495
p-cyano **40**	0.5843	0.5919	−0.3224	0.2989
m-cyano **41**	0.5980	0.5932	−0.3266	0.2875

Upon inspection of the source of the inhibition of the phenylbutene rate, it is seen that the total rate of decay is comparable to other members of the series (note Table II). However, the quantum yield is ca. 10-fold lower (ϕ = 0.0058) than the other arylbutenes. In using eq 5 we obtain ^1k_r as a product of $^1k_{dtot}$ and $^1\phi_r$. Here $^1\phi_r$ is the probability of the excited singlet going on to product as compared with other singlet processes, and this must be quite low for the phenylbutene singlet ^{1}**3**.

In our previous studies[22,23,27] evidence accumulated that it is generally S_0 of the cyclopropyldicarbinyl diradical which reverts to the di-π-methane reactant by bond 2,3 fission of the 1,4-diradical, while S_1 tends to bicycle onward to the vinyl- or arylcyclopropane which is the di-π-methane rearrangement product. In the example under discussion the low quantum yield, coupled with normal vertical singlet rates of decay, suggests that with phenyl substitution one obtains greater radiationless decay of the S_1 to S_0 cyclopropyldicarbinyl diradical relative to conversion onward to product.

An understanding of this effect comes with the realization that the cyclopropyldicarbinyl diradical provides an ideal pathway for radiationless decay along the reaction hypersurface. Any such S_1 diradicals which decay to S_0 cyclopropyldicarbinyl diradicals can be expected to revert to di-π-methane reactant, since previous studies[22,23] have shown that the ground-state cyclopropyldicarbinyl diradicals undergo central bond fission in a Grob type fragmentation.

The question, then, is why the parent hydrocarbon di-π-methane **3** would afford a cyclopropyldicarbinyl diradical (i.e., **37**) more disposed to undergo radiationless decay. The SCF–CI calculations revealed an interesting phase relationship of the carbinyl carbons 1 and (e.g.) 8 whereby

---

(25) (a) Zimmerman, H. E.; Gruenbaum, W. T.; Klun, R. T.; Steinmetz, M. G.; Welter, T. R. *J. Chem. Soc., Chem. Commun.* **1978**, 228–230. (b) Zimmerman, H. E.; Steinmetz, M. G. *Ibid.* **1978**, 231–232.

(26) Zimmerman, H. E.; Klun, R. T. *Tetrahedron* **1978**, *43*, 1775–1803.

(27) (a) Zimmerman, H. E. *Chimia* **1982**, *36*, 423–428. (b) Zimmerman, H. E. *Acc. Chem. Res.* **1982**, *10*, 312–317. (c) Zimmerman, H. E. *Top. Curr. Chem.* **1982**, *100*, 45–73. (d) Zimmerman, H. E.; Cutler, T. P. *J. Org. Chem.* **1978**, *43*, 3283–3303.

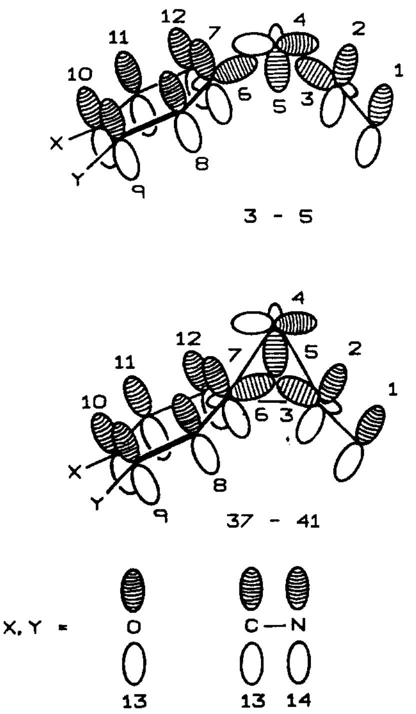


Figure 2. Basis orbitals in reactant and bridged species.

Table X. S_1 Diradical Bond Orders Involving the Carbinyl Carbon 1

	bond orders for the diradicals				
overlap	parent 37	p-MeO 38	*m*-MeO 39	*p*-CN 40	*m*-CN 41
1-2	0.4903	0.4984	0.4933	0.5146	0.5042
1-3	0.0092	0.0050	0.0068	−0.0027	0.0031

these have SCF LCAO MO coefficients of opposite sign in HOMO and like sign in LUMO; note Table IX and Figure 2. This pattern reminds us of the situation in simple ethylenes.[28a] Thus twisting provides a mode of radiationless decay in (e.g.) stilbene.[28b,c]

In the present instance, twisting about bond 1,2 offers a means of diminishing antibonding interactions. Table X gives the S_1 bond orders for overlap between p orbitals 1 and 2 as well as the potential bond orders between orbitals 1 and 3 resulting from twisting.

Inspection of Table X reveals that the parent diradical **37** has the most antibonding 1,2-character and the most potentially bonding 1,3-character. Hence this diradical has the most energetically to gain by twisting. The suggestion that the low quantum yield and low effective S_1 reaction rate come from partition heavily favoring diradical reversion to phenylbutene reactant **3** thus is supported. Interestingly, the most reactive di-π-methane system is the *p*-cyano butene **5a**, and reference to Table X shows the corresponding S_1 diradical to have the least antibonding 1,2-overlap and the least bonding 1,3-overlap. This suggests the enhanced reactivity derives at least in part from less efficient radiationless decay of the diradical in this case.

Discussion of the Arylcyclopropane Photochemistry. The cyclopropane photochemistry consisted of two types of processes in addition to Griffin[29] carbene fragmentation. The first consisted of the well-known[3h,3i,30,31b] 1,4-hydrogen transfer of the 1,3-diradicals as shown in eq 11.

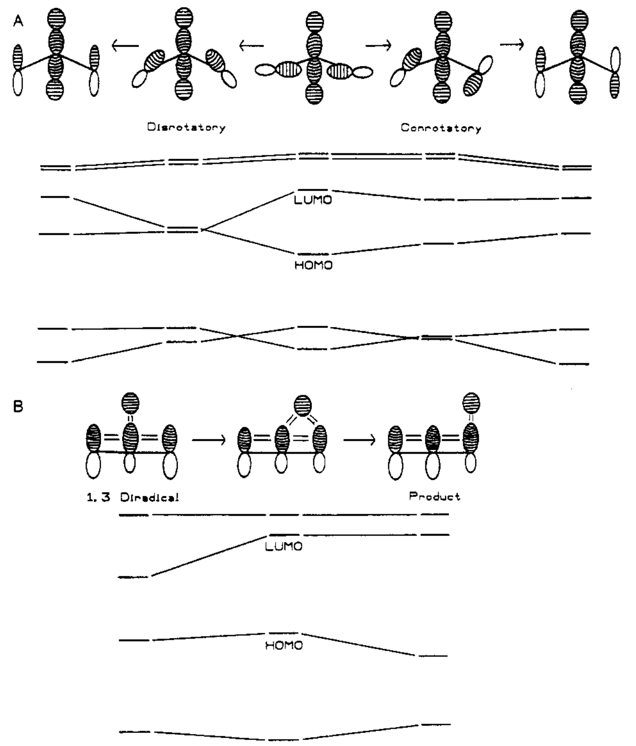
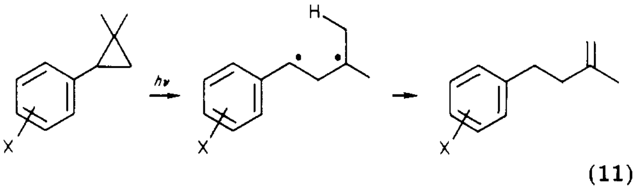
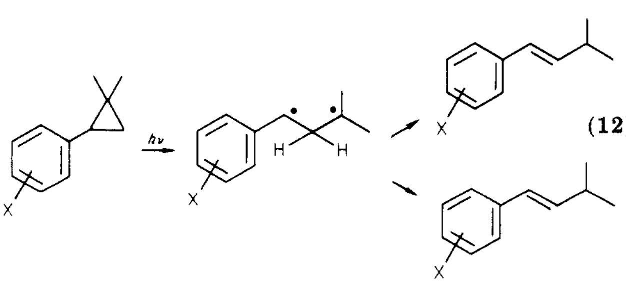


Figure 3. (a) Correlation diagram for cyclopropane opening. (b) Correlation diagram for 1,3-diradical rearrangement.



(11)

The second type of product results from a 1,2-shift of a hydrogen at carbon 2 of the 1,3-diradical to carbon 1 or 3 in a process which appears to derive from S_1. Such migrations are quite rare.[22,23,30,31] However, hydrogen shifts[30,31] have been observed in three-membered ring openings and vinyl shifts have been encountered in our earlier investigations.[22,23]



(12)

An understanding of this intriguing reaction derives from the MO following correlation diagrams in Figure 3a,b. These are drawn paraphrasing both Hückel and SCF

---

[28] (a) Merer, A. J.; Mulliken, C. C. J. *Chem. Rev.* **1969**, *69*, 639–656. (b) Hammond, G. S.; Saltiel, J.; Lamola, A. A.; Turro, N. J.; Bradshaw, J. S.; Cowan, D. O.; Counsell, R. C.; Vogt, V.; Dalton, C. *J. Am. Chem. Soc.* **1964**, *86*, 3197–3217.

[29] (a) Griffin, G. W. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 537–547. (b) Richardson, D. B.; Durett, L. R.; Martin, J. M.; Putnam, W. E.; Slaymaker, S. C.; Dvoretsky, I. *J. Am. Chem. Soc.* **1965**, *87*, 2763–2765.

[30] (a) Mazzocchi, P. H.; Lustig, R. S. *J. Am. Chem. Soc.* **1975**, *97*, 3707–3713. (b) Mazzochi, P. H.; Lustig, R. S. *Ibid.* **1975**, *97*, 3714–3718.

[31] (a) Griffin, G. W.; Covell, J.; Petterson, R. C.; Dodson, R. M.; Klose, G. *J. Am. Chem. Soc.* **1965**, *87*, 1410–1411. (b) Griffin, G. W.; Kristensson, H. *Tetrahedron Lett.* **1966**, 3259–3265. (c) Mazzochi, P. H.; Lustig, R. S.; Craig, G. W. *J. Am. Chem. Soc.* **1970**, *92*, 2169–2170.

calculations. Our first conclusion derives from the correlation diagram for rearrangement of the 1,3-diradical **42** (note Figure 3b). It is seen that there is no HOMO–LUMO crossing and the reaction is thermally allowed but excited state forbidden in the sense that there is no crossing to afford a bifunnel[22,27b,27c,32] leading to ground-state product. However, Figure 3a describing the three-membered ring opening reveals that the disrotatory three-membered ring opening involves a HOMO–LUMO crossing. The correlation agrees with the work of Hoffmann[33] which predicted a conrotatory thermal opening of cyclopropane.

In the present instance, a disrotatory opening followed by the 1,2-hydrogen shift will be photochemically allowed. In ground-state chemistry we have the oft followed rule that an even number of forbidden reactions, when joined into one concerted process, will be allowed while an odd number of forbidden reactions so superimposed will be forbidden; also any combination of allowed reactions will be allowed. The rule applies only where HOMO and LUMO orbitals correlate HOMO–LUMO or HOMO–HOMO and LUMO–LUMO. In excited-state chemistry the rule needs modification. Then one allowed (ground state forbidden) portion of the reaction, here disrotatory opening, is needed to provide a bifunnel and allowedness for the reaction. This is independent of whether the 1,3-diradical **42** is a discrete intermediate or, instead, hydrogen migration begins to occur as soon as three-membered ring opening is appreciable.

Conclusion

We note that, despite very extensive efforts in studying the di-π-methane rearrangement since our initial description, the reaction still presents surprises and novel chemistry. The ultimate goal in organic photochemistry is bringing the field to the point where each new result is an expected one.

Experimental Section

General Experimental Procedures. All reactions were run under dry nitrogen. Tetrahydrofuran (THF) (Fisher, histological grade) was distilled from lithium aluminum hydride and benzophenone ketyl. Standard workup A involved dilution with water, ether extraction, and washing the ether extracts with water and brine followed by drying and concentration in vacuo. Standard work up B was the same except pentane was used for extraction. Column chromatography was performed on slurry packed quartz columns with silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) or alumina (Fisher, 80–200 mesh) packing mixed with Sylvania 2282 phosphor to permit UV monitoring of bands. Vapor phase chromatography was performed with column A, 0.64 × 150 cm packed with 10% QF-1 on 100–200 mesh Varaport 30, or column B, 0.48 × 305 cm packed with 10% QF-1 on 60–80 mesh Chromosorb W.

3-Methyl-3-(*p*-methoxyphenyl)-1-butene. To a slurry of 25.9 g (72.4 mmol) of methyltriphenylphosphonium bromide in 100 mL of THF was added 48.3 mL (72.4 mmol) of 1.5 M *n*-butyllithium in hexane; 8.6 g (48.3 mmol) of 2-methyl-2-(*p*-methoxyphenyl)-1-propanal[34] in 50 mL of THF was then added over 15 min followed by stirring for 4 h. Workup B afforded 10 g of an oil. Chromatography on a 3 × 91 cm silica gel column eluted with 10% ether in hexane gave after 350 mL 5.9 g (69%) of the olefin as a colorless oil pure by NMR. The spectral data: NMR (CCl_4) δ 7.15 (d, J = 9.0 Hz, 2 H, Ar), 6.71 (d, J = 9.0 Hz, 2 H, Ar), 5.98 (dd, J = 10.5 Hz, 17.4 Hz, 1 H, C=CH), 4.96 (m, 2 H, $C=CH_2$), 3.73 (s, 3 H, CH_3O), 1.38 (s, 6 H, CH_3); IR (thin film) 3086, 3067, 3040, 3003, 2967, 2941, 2915, 2841, 1642, 1621, 1580, 1513, 1462, 1445, 1410, 1376, 1359, 1248, 1181, 1033, 1003, 824, 785 cm^{-1}; MS, *m/e* 176.1201; calcd for $C_{12}H_{16}O$, *m/e* 176.1201; UV (95% ethanol) 276 nm (ε 1777), 283 (1537).

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.67; H, 9.31.

3-Methyl-3-(*m*-methoxyphenyl)-1-butene. To a slurry of 32.6 g (80.8 mmol) of methyltriphenylphosphonium iodide in 200 mL of THF was added 53.9 mL (80.8 mmol) of 1.5 M *n*-butyllithium in hexane. A solution of 12.0 g (67.3 mmol) of 2-methyl-2-(*m*-methoxyphenyl)-1-propanal[34] in 50 mL of THF was added over 40 min. The mixture was stirred for 14 h. Workup B with hexane as solvent afforded a yellow oily solid. Chromatography on a 4 × 78 cm silica gel column eluted with hexane afforded after 1250 mL 9.5 g of a clear oil which was distilled (46–48 °C (0.05 torr)) to yield 8.4 g (71%) of olefin as clear oil. The spectral data: NMR ($CDCl_3$) δ 7.36 (m, 1 H, Ar), 6.87 (m, 3 H, Ar), 6.15 (dd, J = 10.5 Hz, 17.4 Hz, 1 H, C=CH), 5.15 (m, 2 H, $C=CH_2$), 3.85 (s, 3 H, CH_3O), 1.41 (s, 6 H, CH_3); IR (thin film) 3086, 3067, 2994, 2976, 2941, 2924, 2882, 2849, 1645, 1618, 1608, 1592, 1493, 1475, 1460, 1441, 1381, 1372, 1326, 1300, 1272, 1236, 1220, 1188, 1117, 1091, 1062, 1013, 923, 892, 787, 717 cm^{-1}; MS, *m/e* 176.1201; calcd for $C_{12}H_{16}O$, *m/e* 176.1197; UV (95% ethanol) 271 nm (ε 1898), 279 (1678).

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.56; H, 8.98.

3-Methyl-3-(*p*-bromophenyl)-1-butene. To a slurry of 26.6 g (74.4 mmol) of methyltriphenylphosphonium bromide in 150 mL of THF was added 49.6 mL (74.4 mmol) of 1.5 M *n*-butyllithium in hexane. A solution of 13.0 g (57.4 mmol) of 2-methyl-2-(*p*-bromophenyl)propanal[34] in 75 mL of THF was added over 30 min. The mixture was stirred for 4 h. Workup B afforded a yellow oily solid which distilled (70–75 °C (0.1 torr)) to yield 10.5 g (81.6%) of olefin as an oil. The spectral data: NMR ($CDCl_3$) δ 7.54 (d, J = 9.0 Hz, 2 H, Ar), 7.19 (d, J = 9.0 Hz, 2 H, Ar), 6.07 (dd, J = 10.5 Hz, 16.5 Hz, 1 H, C=CH), 5.10 (m, 2 H, $C=CH_2$), 1.37 (s, 6 H, CH_3); IR (thin film) 3077, 2967, 2924, 2874, 1639, 1595, 1495, 1479, 1471, 1420, 1401, 1381, 1364, 1241, 1110, 1100, 1080, 1045, 1015, 1005, 920, 830, 730 cm^{-1}; MS, *m/e* 224.0201; calcd for $C_{11}H_{13}Br$, *m/e* 224.0200.

Anal. Calcd for $C_{11}H_{13}Br$: C, 58.69; H, 5.82. Found: C, 58.86; H, 5.91.

3-Methyl-3-(*p*-cyanophenyl)-1-butene. A mixture of 4.26 g (18.9 mmol) of 3-methyl-3-(*p*-bromophenyl)-1-butene and 2.20 g (24.6 mmol) of cuprous cyanide in 40 mL of *N*-methyl-2-pyrrolidone was heated under nitrogen to 175 °C for 4.5 h. The reaction was cooled, poured into 200 mL of 5% sodium cyanide, and ether extracted. The ether solution was washed with 200 mL of 5% sodium cyanide, water, and brine, dried, and concentrated in vacuo to afford 3.6 g of brown oil. Chromatography on a 3 × 74 cm silica gel column eluted with 10% ether in hexane afforded after 750 mL 2.8 g of clear oil which was molecularly distilled (60–80 °C (1 torr)) to yield 2.5 g (77%) of nitrile as clear oil. The spectral data: NMR ($CDCl_3$) δ 7.46 (d, J = 9.0 Hz, 2 H, Ar), 7.32 (d, J = 9.0 Hz, 2 H, Ar), 5.90 (dd, J = 10.5 Hz, 16.5 Hz, 1 H, C=CH), 5.00 (m, 2 H, $C=CH_2$), 1.36 (s, 6 H, CH_3); IR (thin film) 3086, 2967, 2933, 2874, 2222, 1645, 1616, 1511, 1475, 1420, 1410, 1391, 1370, 1245, 1125, 1100, 1050, 1030, 1015, 930, 850, 745, 700 cm^{-1}; MS, *m/e* 171.1047; calcd for $C_{12}H_{13}N$, *m/e* 171.1045.

Anal. Calcd for $C_{12}H_{13}N$: C, 84.17; H, 7.65. Found: C, 84.32; H, 7.68.

2-Methyl-2-(*m*-bromophenyl)propionitrile. To a slurry of 39.8 g (355 mmol) potassium *tert*-butoxide in 500 mL of ether at −72 °C was added a solution of 26.7 g (136 mmol) of *m*-bromophenylacetonitrile[35] and 22.9 mL (355 mmol) of methyl iodide in 50 mL of THF over 30 min. The reaction was stirred 1 h at room temperature, washed with water and brine, dried, and concentrated in vacuo to afford 28.3 g of oil which was distilled (79–81 °C (0.15 torr)) to yield 19.9 g (65%) of nitrile. The spectral data: NMR ($CDCl_3$) δ 7.30 (m, 4 H, Ar), 1.66 (s, 6 H, CH_3); IR (thin film) 3067, 2994, 2941, 2882, 2247, 1600, 1575, 1481, 1473, 1462, 1422, 1376, 1247, 1205, 1122, 1098, 1082, 1003, 942, 888, 856, 795, 732, 702, 665 cm^{-1}; MS, *m/e* 222.9996; calcd for $C_{10}H_{10}BrN$, *m/e* 222.9995.

---

[32] Michl, J. *Mol. Photochem.* **1972**, *4*, 243–255.

[33] Hoffmann, R. *J. Am. Chem. Soc.* **1968**, *90*, 1475–1485.

[34] Kantzel, H.; Wolf, H.; Schaffner, K. *Helv. Chim. Acta* **1971**, *54*, 868–897.

[35] Parham, W. E.; Jones, L. D. *J. Org. Chem.* **1976**, *41*, 1187–1189.

Anal. Calcd for $C_{10}H_{10}BrN$: C, 53.60; H, 4.50. Found: C, 53.60; H, 4.46.

2-Methyl-2-(*m*-bromophenyl)propanal. A solution of 24.0 g (107 mmol) of 2-methyl-2-(*m*-bromophenyl)propionitrile in 150 mL of hexane was cooled to 0 °C, and 145 mL (139 mmol) of 0.96 M diisobutylaluminum hydride was added over 40 min. The reaction was stirred for 30 min at 0 °C and 2 h at room temperature, quenched with 15 mL of 5% hydrochloric acid, filtered through Celite, and concentrated in vacuo to afford a yellow oil. The oil was dissolved in 500 mL of THF, 50 mL of water, and 10 mL of concentrated sulfuric acid and was stirred for 16 h. Workup A afforded 22.2 g (99%) of aldehyde as clear oil pure by NMR. The spectral data: NMR ($CDCl_3$) δ 9.46 (s, 1 H, CHO), 7.30 (m, 4 H, Ar), 1.44 (s, 6 H, CH_3); IR (thin film) 3058, 2967, 2933, 2874, 2801, 2703, 1727, 1592, 1565, 1477, 1414, 1364, 1242, 1095, 1076, 999, 915, 885, 848, 787, 763, 698, 673 cm^{-1}; MS, *m/e* 225.9993; calcd for $C_{10}H_{11}OBr$, *m/e* 225.9993.

Anal. Calcd for $C_{10}H_{11}OBr$: C, 52.89; H, 4.88. Found: C, 52.78; H, 4.85.

3-Methyl-3-(*m*-bromophenyl)-1-butene. To a slurry of 46.3 g (114 mmol) of methyltriphenylphosphonium iodide in 500 mL of THF was added 73.4 mL (110 mmol) of 1.5 M *n*-butyllithium in hexane. A solution of 20.0 g (88.1 mmol) of 2-methyl-2-(*m*-bromophenyl)-1-propanal in 50 mL of THF was added over 30 min. The solution was stirred for 14 h. Workup B afforded a yellow oily solid. Chromatography on a 5 × 55 cm silica gel column eluted with hexane afforded after 1000 mL 12.0 g (60%) of olefin pure by NMR. The spectral data: NMR ($CDCl_3$) δ 7.25 (m, 4 H, Ar), 5.94 (dd, J = 9.90 Hz, 16.80 Hz, 1 H, C═CH), 5.01 (m, 2 H, $C{=}CH_2$), 1.41 (s, 6 H, CH_3); IR (thin film) 3086, 2967, 2933, 2874, 1642, 1600, 1567, 1481, 1471, 1410, 1385, 1368, 1238, 1079, 1002, 922, 885, 852, 790, 745, 707 cm^{-1}; MS, *m/e* 224.0201; calcd for $C_{11}H_{13}Br$, *m/e* 224.0200.

Anal. Calcd for $C_{11}H_{13}Br$: C, 58.69; H, 5.82. Found: C, 58.86; H, 6.00.

3-Methyl-3-(*m*-cyanophenyl)-1-butene. A mixture of 7.0 g (31.1 mmol) of 3-methyl-3-(*m*-bromophenyl)-1-butene and 3.6 g (40.4 mmol) of cuprous cyanide in 75 mL of *N*-methyl-2-pyrrolidone was heated under nitrogen to 175–180 °C for 6 h. The cooled mixture was poured into 400 mL of 5% sodium cyanide and extracted with ether. The ether solution was washed with 350 mL of 5% sodium cyanide, water, and brine, dried, and concentrated in vacuo to afford 4.9 g of brown oil. Chromatography on a 4 × 89 cm silica gel column eluted with 10% ether in hexane afforded after 1500 mL 3.8 g of clear oil which molecularly distilled (60–80 °C (1 torr)) to yield 3.5 g (66%) of nitrile. The spectral data: NMR ($CDCl_3$) δ 7.40 (m, 4 H, Ar), 6.94 (dd, J = 11.10 Hz, 17.10 Hz, 1 H, C═CH), 5.00 (m, 2 H, $C{=}CH_2$), 1.38 (s, 6 H, CH_3); IR (thin film) 3096, 2976, 2941, 2882, 2232, 1645, 1605, 1587, 1490, 1425, 1389, 1370, 1285, 1264, 1181, 1095, 1045, 1005, 920, 802, 693 cm^{-1}; MS, *m/e* 171.1047; calcd for $C_{12}H_{13}N$, *m/e* 171.1048.

Anal. Calcd for $C_{12}H_{13}N$: C, 84.17; H, 7.65. Found: C, 84.19; H, 7.73.

1,1-Dimethyl-2-(*m*-methoxyphenyl)cyclopropane. When a modification of the method of Olofson[36] was used, 100 mL of isobutene was condensed with dry ice cooling into a 500-mL 3-neck flask fitted with dry ice cold finger condenser, 9.0 g (57.5 mmol) of *m*-methoxybenzyl chloride[37] was added, and the cooling was removed. To this was added over 1 h 72.3 mL (57.5 mmol) of a 0.80 M solution of lithium 2,2,6,6-tetramethylpiperidide in ether prepared by adding 38.3 mL of 1.5 M *n*-butyllithium to 8.12 g (57.5 mmol) mL of 2,2,6,6-tetramethylpiperidine in 72 mL of ether. The mixture was refluxed for 8 h, poured into water, and ether extracted, and the extracts were washed with 5% hydrochloric acid and water, dried, and concentrated in vacuo to afford 8.9 g of brown oil. Chromatography on a 5 × 54 cm alumina column eluted with 10% ether in hexane afforded after 500 mL 3.0 g of a clear oil which was molecularly distilled (50–70 °C (1 torr)) to yield 2.7 g (27%) of cyclopropane. The spectral data: NMR ($CDCl_3$) δ 7.20 (m, 1 H, Ar), 6.76 (m, 3 H, Ar), 3.80 (s, 3 H, CH_3O), 1.84 (m, 1 H, CH), 1.20 (s, 3 H, CH_3), 0.84 (s, 3 H, CH_3), 0.72 (m, 2 H, CH_2); IR (thin film) 3067, 3003, 2950, 2874, 2833, 2740, 1610, 1587, 1495, 1458, 1439, 1381, 1319, 1295, 1277, 1253, 1203, 1178, 1168, 1130, 1056, 973, 883, 790, 735, 701 cm^{-1}; MS, *m/e* 176.1201; calcd for $C_{12}H_{16}O$, *m/e* 176.1197.

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.80; H, 9.46.

1,1-Dimethyl-2-(*p*-bromophenyl)cyclopropane. When a modification of the method of Olofson[36] was used, 160 mL of isobutene was condensed with dry ice cooling into a 500-mL 3-neck flask fitted with dry ice cold finger condenser, 20.0 g (80.0 mmol) of *p*-bromobenzyl bromide[38] in 35 mL of ether was added, and the cooling was removed. To this was added over 2 h 100 mL (80.0 mmol) of a 0.80 M solution of lithium 2,2,6,6-tetramethylpiperidide in ether (prepared as above). The mixture was refluxed for 2 h, poured into water, and ether extracted, and the extracts were washed with 5% hydrochloric acid and water, dried, and concentrated in vacuo to afford 17.5 g of brown oil. Chromatography on a 4 × 62 cm alumina column eluted with pentane afforded after 500 mL 4.9 g of a clear oil which was molecularly distilled (60–80 °C (1 torr)) to yield 4.4 g (24%) of cyclopropane. The spectral data: NMR ($CDCl_3$) δ 7.25 (d, J = 8.4 Hz, 2 H, Ar), 6.89 (d, J = 8.4 Hz, 2 H, Ar), 1.77 (m, 1 H, CH), 1.04 (s, 3 H, CH_3), 1.02 (m, 2 H, CH_2), 0.70 (s, 3 H, CH_3); IR (thin film) 3067, 3003, 2959, 2933, 2890, 2874, 1499, 1471, 1460, 1406, 1387, 1220, 1130, 1088, 1022, 839, 785, 768, 730 cm^{-1}; MS, *m/e* 224.0201; calcd for $C_{11}H_{13}Br$, *m/e* 224.0198.

Anal. Calcd for $C_{11}H_{13}Br$: C, 58.69; H, 5.82. Found: C, 58.73; H, 5.95.

1,1-Dimethyl-2-(*p*-cyanophenyl)cyclopropane. A mixture of 4.0 g (17.8 mmol) of 1,1-dimethyl-2-(*p*-bromophenyl)cyclopropane and 2.1 g (23.5 mmol) of cuprous cyanide in 40 mL of *N*-methyl-2-pyrrolidone was heated to 170–175 °C for 7 h. The mixture was cooled, poured into 200 mL of 5% sodium cyanide, and ether extracted. The ether extracts were washed with 200 mL of 5% sodium cyanide, water, and brine, dried, and concentrated in vacuo to afford 3.2 g of brown oil. Chromatography on a 3 × 77 cm silica gel column eluted with 5% ether in pentane afforded after 500 mL 2.6 g of clear oil which was molecularly distilled (70–90 °C (1 torr)) to yield 2.3 g (76%) of cyclopropane. The spectral data: NMR ($CDCl_3$) δ 7.50 (d, J = 8.4 Hz, 2 H, Ar), 7.18 (d, J = 8.4 Hz, 2 H, Ar), 1.79 (m, 1 H, CH), 1.22 (s, 3 H, CH_3), 0.85 (m, 2 H, CH_2), 0.76 (s, 3 H, CH_3); IR (thin film) 3067, 3003, 2950, 2924, 2890, 2874, 2237, 1613, 1513, 1456, 795, 748 cm^{-1}; MS, *m/e* 171.1047; calcd for $C_{12}H_{13}N$, *m/e* 171.1045.

Anal. Calcd for $C_{12}H_{13}N$: C, 84.17; H, 7.65. Found: C, 84.40; H, 7.70.

1,1-Dimethyl-2-(*m*-bromophenyl)cyclopropane. When a modification of the method of Olofson[36] was used, 170 mL of isobutene was condensed with dry ice cooling into a 500-mL 3-neck flask fitted with dry ice cold finger condenser, 22.0 g (107 mmol) of *m*-bromobenzyl chloride[39] was added, and the cooling was removed. To this was added over 1 h 133.8 mL (107 mmol) of a 0.80 M solution of lithium 2,2,6,6-tetramethylpiperidide in ether. The mixture was refluxed for 8 h, poured into water, and ether extracted. The extracts were washed with 5% hydrochloric acid and water, dried, and concentrated in vacuo to afford 21.0 g of brown oil. Chromatography on a 5 × 56 cm alumina column eluted with hexane afforded after 900 mL 4.9 g of a clear oil which was distilled (60–70 °C (1 torr)) to yield 4.3 g (18%) of cyclopropane. The spectral data: NMR ($CDCl_3$) δ 7.13 (m, 4 H, Ar), 1.82 (m, 1 H, CH), 1.18 (s, 3 H, CH_3), 0.77 (s, 3 H, CH_3), 0.70 (m, 2 H, CH_2); IR (thin film) 3067, 2985, 2941, 1172, 1127, 1080, 1060, 1043, 1002, 960, 945, 913, 888, 852, 799 cm^{-1}; MS, *m/e* 224.0201; calcd for $C_{11}H_{13}Br$, *m/e* 224.0198.

Anal. Calcd for $C_{11}H_{13}Br$: C, 58.69; H, 5.82. Found: C, 58.79; H, 5.98.

1,1-Dimethyl-2-(*m*-cyanophenyl)cyclopropane. A mixture of 3.8 g (16.9 mmol) of 1,1-dimethyl-2-(*m*-bromophenyl)cyclopropane and 1.96 g (21.9 mmol) of cuprous cyanide in 40 mL of *N*-methyl-2-pyrrolidone was heated to 170–180 °C for 4.5 h. The mixture was cooled, poured into 200 mL of 5% sodium cyanide, and extracted with ether. The ether solution was washed with

---

[36] (a) Olofson, R. A.; Dougherty, C. M. *J. Am. Chem. Soc.* **1976**, *95*, 581–582.

[37] Cornforth, J. W.; Robinson, R. *J. Chem. Soc.* **1942**, 684–689.

[38] Weizmann, M.; Patai, S. *J. Am. Chem. Soc.* **1946**, *68*, 150–151.

[39] Kessar, S. V.; Narula, S.; Gandhi, S. S.; Nadir, U. K. *Tetrahedron Lett.* **1974**, 2906–2906.

200 mL of 5% sodium cyanide, water, and brine, dried, and concentrated in vacuo to afford 3.0 g of brown oil. Chromatography on a 4 × 89 cm silica gel column eluted with 10% ether in hexane afforded after 1450 mL 2.4 g of clear oil which was molecularly distilled (50–65 °C (1 torr)) to yield 2.1 g (73%) of cyclopropane. The spectral data: NMR ($CDCl_3$) δ 7.44 (m, 4 H, Ar), 1.96 (m, 1 H, CH), 1.20 (s, 3 H, CH_3), 0.88 (m, 2 H, CH_2), 0.76 (s, 3 H, CH_3); IR (thin film) 3067, 2994, 2950, 2874, 2740, 2237, 1605, 1582, 1488, 1456, 1431, 1383, 1316, 1287, 1267, 1238, 1166, 1130, 1110, 1091, 1067, 1046, 1004, 967, 915, 901, 873, 825, 802, 723, 708, 695 cm^{-1}; MS, *m/e* 171.1047; calcd for $C_{12}H_{13}N$, *m/e* 171.1045.

Anal. Calcd for $C_{12}H_{13}N$: C, 84.17; H, 7.65. Found: C, 84.08; H, 7.60.

2-Methyl-4-(*p*-methoxyphenyl)-1-butene. To a slurry of 3.0 g (8.42 mmol) of methyltriphenylphosphonium bromide in 100 mL of THF was added 5.24 mL (7.85 mmol) of 1.5 M *n*-butyllithium in hexane. A solution of 1.0 g (5.61 mmol) of 4-(*p*-methoxyphenyl)-2-butanone in 30 mL of THF was added. The mixture was stirred for 4 h. Workup B afforded an oil. Chromatography on a 4 × 84 cm silica gel column eluted with 5% ether in hexane afforded after 1500 mL 700 mg (71%) of olefin. The spectral data: NMR ($CDCl_3$) δ 7.14 (d, J = 9.0 Hz, 2 H, Ar), 6.85 (d, J = 9.0 Hz, 2 H, Ar), 4.76 (s, 2 H, C=CH_2), 3.80 (s, 3 H, CH_3O), 3.73 (m, 2 H, CH_2), 2.34 (m, 2 H, CH_2), 1.79 (s, 3 H, CH_3); IR (thin film) 3086, 3049, 3012, 2950, 2874, 2849, 1653, 1610, 1582, 1511, 1453, 1370, 1297, 1242, 1172, 1103, 1035, 883, 853, 816, 803, 740 cm^{-1}; MS, *m/e* 176.1201; calcd for $C_{12}H_{16}O$, *m/e* 176.1201.

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.52; H, 9.12.

2-Methyl-4-(*p*-cyanophenyl)-1-butene. To a slurry of 7.14 g (20.0 mmol) of methyltriphenylphosphonium bromide in 25 mL of THF was added 12.8 mL (19.2 mmol) of 1.5 M *n*-butyllithium in hexane. A solution of 2.77 g (16.0 mmol) of 4-(*p*-cyanophenyl)-2-butanone[40] in 25 mL of THF was added. The mixture was stirred for 4 h. Workup A afforded 4.1 g of brown oil. Chromatography on a 3 × 97 cm silica gel column eluted with 5% ether in hexane afforded after 1150 mL 1.23 g of oil which was molecularly distilled (80–100 °C (1 torr)) to yield 0.74 g (27%) of olefin. The spectral data: NMR ($CDCl_3$) δ 7.43 (d, J = 8.1 Hz, 2 H, Ar), 7.20 (d, J = 8.1 Hz, 2 H, Ar), 4.69 (s, 1 H, C=CH), 4.62 (s, 1 H, C=CH), 2.75 (m, 2 H, CH_2), 2.27 (m, 2 H, CH_2), 1.74 (s, 6 H, CH_3); IR (thin film) 3067, 3030, 2967, 2933, 2857, 2232, 1647, 1608, 1506, 1449, 1416, 1377, 1294, 1181, 1115, 1036, 895, 868, 828 cm^{-1}; MS, *m/e* 171.1047; calcd for $C_{12}H_{13}N$, *m/e* 171.1045.

Anal. Calcd for $C_{12}H_{13}N$: C, 84.17; H, 7.65. Found: C, 84.15; H, 7.71.

4-(*m*-Bromophenyl)-2-butanone. To 29.2 mmol of ethanolic sodium ethoxide, prepared from 20 mL of absolute ethanol and 0.67 g (29.2 mmol) of sodium, was added 3.80 g (29.2 mmol) of ethyl acetoacetate. After 30 min, 6.0 g (29.2 mmol) of *m*-bromophenyl chloride[39] was added, and this was refluxed for 1.5 h. Then 2.4 g of sodium hydroxide in 15 mL of water was added and the mixture was refluxed for 4 h. Then the mixture was acidified to pH 2 with 40% phosphoric acid. Workup A afforded 6.5 g of oil. Chromatography on a 4 × 87 cm silica gel column eluted with 5% ether in hexane afforded after 700 mL a clear oil which was distilled (95–97 °C (0.2 torr)) to yield 3.1 g (47%) of butanone. The spectral data: NMR ($CDCl_3$) δ 7.30–7.03 (m, 4 H, Ar), 2.76 (m, 4 H, CH_2), 2.14 (s, 6 H, CH_3); IR (thin film) 3049, 2994, 2907, 1715, 1592, 1515, 1473, 1425, 1408, 1364, 1203, 1161, 1072, 998, 888, 859, 820, 780, 692, 668 cm^{-1}; MS, *m/e* 225.9993; calcd for $C_{10}H_{11}OBr$, *m/e* 225.9993.

Anal. Calcd for $C_{10}H_{11}OBr$: C, 52.89; H, 4.88. Found: C, 52.85; H, 4.87.

2-Methyl-4-(*m*-bromophenyl)-1-butene. To a slurry of 4.27 g (10.6 mmol) of methyltriphenylphosphonium iodide in 10 mL of THF was added 7.1 mL (10.6 mmol) of 1.5 M *n*-butyllithium and the mixture was stirred for 20 min. A solution of 2.0 g (8.81 mmol) of 4-(*m*-bromophenyl)-2-butanone in 10 mL of THF was added over 15 min. The mixture was stirred for 5 h. Workup B afforded 2.0 g of yellow oil. Chromatography on a 4 × 50 cm silica gel column eluted with hexane afforded after 1200 mL a clear oil which was molecularly distilled (60–75 °C (1 torr)) to yield 1.31 g (66%) of olefin. The spectral data: NMR ($CDCl_3$) δ 7.31–7.05 (m, 4 H, Ar), 4.73 (s, 1 H, C=CH), 4.69 (s, 1 H, C=CH), 2.68 (m, 2 H, CH_2), 2.25 (m, 2 H, CH_2), 1.07 (s, 6 H, CH_3); IR (thin film) 3067, 2967, 2849, 1645, 1599, 1567, 1475, 1447, 1425, 1374, 1205, 1166, 1073, 1000, 890, 830, 810, 782, 693, 670 cm^{-1}; MS, *m/e* 224.0201; calcd for $C_{11}H_{13}Br$, *m/e* 224.0200.

Anal. Calcd for $C_{11}H_{13}Br$: C, 58.69; H, 5.82. Found: C, 58.90; H, 5.75.

2-Methyl-4-(*m*-cyanophenyl)-1-butene. A mixture of 1.0 g (4.44 mmol) of 2-methyl-4-(*m*-bromophenyl)-1-butene and 0.52 g (5.77 mmol) of cuprous cyanide in 20 mL of *N*-methyl-2-pyrrolidone was heated under nitrogen to 175–185 °C for 5 h. The mixture was cooled, poured into 25 mL of 5% aqueous sodium cyanide, and ether extracted. The extracts were washed with 25 mL of 5% aqueous sodium cyanide and water, dried, and concentrated in vacuo to afford 0.99 g of brown oil. Chromatography on a 4 × 70 cm silica gel column eluted with hexane afforded after 200 mL 0.90 g of olefin as clear oil pure by NMR. The spectral data: NMR ($CDCl_3$) δ 7.38 (m, 4 H, Ar), 4.72 (s, 1 H, C=CH), 5.66 (s, 1 H, C=CH), 2.73 (m, 2 H, CH_2), 2.27 (m, 2 H, CH_2), 1.79 (s, 6 H, CH_3); MS, *m/e* 171.1047; calcd for $C_{12}H_{13}N$, *m/e* 171.1048.

Anal. Calcd for $C_{12}H_{13}N$: C, 84.17; H, 7.65. Found: C, 84.26; H, 7.58.

2-Methyl-4-(*m*-methoxyphenyl)-2-butene. To a slurry of 3.45 g (7.99 mmol) of isopropyltriphenylphosphonium iodide in 100 mL of THF was added 5.32 mL (7.99 mmol) of 1.5 M *n*-butyllithium in hexane. A solution of 1.00 g (6.66 mmol) of *m*-methoxyphenylacetaldehyde[41] in 75 mL of THF was added over 30 min. The mixture was stirred for 4 h. Workup B afforded 2.04 g of yellow oil. Chromatography on a 3 × 55 cm silica gel column eluted with 10% ether in hexane afforded after 450 mL 700 mg (60%) of olefin as clear oil. The spectral data: NMR ($CDCl_3$) δ 7.17 (m, 1 H, Ar), 6.79 (m, 3 H, Ar), 5.36 (m, 1 H, C=CH), 3.85 (s, 3 H, CH_3O), 3.33 (d, J = 8.1 Hz, 2 H, CH_2), 1.77 (d, J = 3.0 Hz, 6 H, CH_3); IR (thin film) 3040, 3012, 2959, 2907, 2849, 2817, 1669, 1600, 1582, 1488, 1464, 1451, 1439, 1379, 1312, 1279, 1256, 1192, 1163, 1148, 1105, 1091, 1052, 998, 988, 945, 880, 857, 843, 789, 746, 735, 695 cm^{-1}; MS, *m/e* 176.1201; calcd for $C_{12}H_{16}O$, *m/e* 176.1201.

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.96; H, 7.29.

2-Methyl-4-(*p*-bromophenyl)-2-butene. To a slurry of 4.34 g (10.0 mmol) of isopropyltriphenylphosphonium iodide in 40 mL of THF was added 6.0 mL (9.04 mmol) of 1.5 M *n*-butyllithium in hexane. A solution of 1.0 g (5.0 mmol) of *p*-bromophenylacetaldehyde[42] in 15 mL of THF was added over 10 min. The mixture was stirred for 2 h. Workup B afforded a brown oil. The oil was bulb-to-bulb distilled (60–80 °C (1 torr)) to afford 0.47 g (42%) of olefin pure by NMR. The spectral data: NMR ($CDCl_3$) δ 7.37 (d, J = 9.0 Hz, 2 H, Ar), 7.01 (d, J = 9.0, 2 H, Ar), 5.27 (t, J = 7.5 Hz, 1 H, C=CH), 3.26 (d, J = 7.5 Hz, 2 H, CH_2), 1.79 (s, 3 H, CH_3), 1.74 (s, 3 H, CH_3); IR (thin film) 3040, 2976, 2924, 1486, 1453, 1443, 1404, 1377, 1198, 1100, 1072, 1010, 925, 860, 810 cm^{-1}; MS, *m/e* 224.0201; calcd for $C_{11}H_{13}Br$, *m/e* 224.0200.

Anal. Calcd for $C_{11}H_{13}Br$: C, 58.69; H, 5.82. Found: C, 58.75; H, 5.82.

2-Methyl-4-(*p*-cyanophenyl)-2-butene. A mixture of 0.47 g (2.1 mmol) of 2-methyl-4-(*p*-bromophenyl)-2-butene and 1.4 g (15.6 mmol) of cuprous cyanide in 10 mL of *N*-methyl-2-pyrrolidone was heated under nitrogen to 180–190 °C for 4 h. The mixture was cooled, poured into 20 mL of 5% aqueous sodium cyanide, and ether extracted, and the extracts were washed with 20 mL of 5% aqueous sodium cyanide, water, and brine, dried, and concentrated in vacuo to afford 284 mg of brown oil. Chromatography on a 2 × 43 cm silica gel column eluted with 10% ether in hexane afforded after 100 mL 260 mg (55%) of olefin as clear oil. The spectral data were as follows: NMR ($CDCl_3$) δ 7.56 (d, J = 9.0 Hz, 2 H, Ar), 7.27 (d, J = 9.0 Hz, 2 H, Ar), 5.29 (t, J = 7.5 Hz, 1 H, C=CH), 3.40 (d, J = 7.5 Hz, 2 H, CH_2), 1.82 (s, 3 H, CH_3), 1.78 (s, 3 H, CH_3); IR (thin film) 3040, 2976, 2933, 2865, 2237, 1610, 1506, 1543, 1443, 1414, 1379, 1181, 1105, 1022,

---

(40) Jones, L. A.; Johnston, R. L. *J. Chem. Eng. Data* **1971**, *16*, 112–115.

(41) Lin, K. H.; Robinson, R. *J. Chem. Soc.* **1938**, 2005–2007.

(42) Hino, T.; Suzuki, T.; Nakagawa, M. *Chem. Pharm. Bull.* **1973**, *21*, 2786–2789.

980, 865, 823 cm^{-1}; MS, *m/e* 171.1047; calcd for $C_{12}H_{13}N$, *m/e* 171.1048.

Anal. Calcd for $C_{12}H_{13}N$: C, 84.17; H, 7.65. Found: C, 84.09; H, 7.89.

***cis*-3-Methyl-1-(*m*-cyanophenyl)-1-butene.** To a slurry of 3.2 g (8.01 mmol) of (2-methylpropyl)triphenylphosphonium bromide in 40 mL of ether was added 5.08 mL (7.63 mmol) of 1.5 M *n*-butyllithium in hexane and this was stirred for 30 min. A solution of 1.0 g (7.63 mmol) of *m*-cyanobenzaldehyde[43] in 40 mL of ether was added over 10 min, and the mixture was stirred for 4 h, then was washed with water and brine, dried, and concentrated in vacuo to afford a yellow oily solid. Chromatography on a 3 × 40 cm silica gel column eluted with 10% ether in hexane afforded after 300 mL 0.97 g of a clear oil. The oil was purified by vapor phase chromatography on column B to afford 460 mg (46%) of olefin. The spectral data: NMR ($CDCl_3$) δ 8.02–7.16 (m, 4 H, Ar), 6.26 (d, $J = 11.5$ Hz, 1 H, C=CH), 5.89 (dd, $J = 11.5$ Hz, 10.3 Hz, 1 H, C=CH), 2.77 (m, 1 H, CH), 1.03 (d, $J = 6.5$ Hz, 6 H, CH_3); IR (thin film) 3058, 3003, 2959, 2924, 2227, 1681, 1608, 1587, 1490, 1475, 1458, 1443, 1403, 1391, 1374, 1311, 1230, 1172, 1110, 1100, 1006, 946, 910, 845, 822, 813, 734, 720, 701, 680 cm^{-1}; MS, *m/e* 171.1047; calcd for $C_{12}H_{13}N$, *m/e* 171.1048.

Anal. Calcd for $C_{12}H_{13}N$: C, 84.17; H, 7.65. Found: C, 84.18; H, 7.46.

General Procedure for Exploratory Photolysis. All photolysis solutions were purged with purified nitrogen[44] for 1 h before irradiation. *tert*-Butyl alcohol used as solvent was distilled from lithium aluminum hydride.

All direct photolyses were performed in *tert*-butyl alcohol by using a 450-W medium-pressure mercury lamp immersion apparatus with a Corex glass filter. After irradiation a portion of the photolysate was analyzed by VPC on column A with naphthalene as an internal standard. Authentic compounds were used as standards. The material not used for analysis was bulb-to-bulb distilled in vacuo (50–70 °C (0.1–0.3 torr)) to collect all volatile compounds which were then separated and isolated by vapor phase chromatography with column B. The nonvolatile residue was investigated by proton NMR and was shown not to contain the isolated reaction products.

All sensitized exploratory photolyses were run on the Black Box apparatus (see below) with acetone (MCB, Reagent ACS) as solvent and sensitizer through filter solution combination A (see below). Analysis was performed as in the direct irradiations above with column A and product isolation was by VPC on column B.

Exploratory Direct Photolysis of 3-Methyl-3-(*p*-methoxyphenyl)-1-butene. Product Isolation and Identification. A solution of 412 mg of 3-methyl-3-(*p*-methoxyphenyl)-1-butene in 450 mL of *tert*-butyl alcohol was irradiated for 8.8 h (77% conversion). Analysis as described above of the photolyzate afforded 90.5 mg (23.1%) of nonvolatile material and the following: 3-methyl-3-(*p*-methoxyphenyl)-1-butene, 88.0 mg (22.5%); 1,1-dimethyl-2-(*p*-methoxyphenyl)cyclopropane,[45] 30.8 mg (7.9%); 2-methyl-4-(*p*-methoxyphenyl)-1-butene, 113.6 mg (29.0%); *cis*-3-methyl-1-(*p*-methoxyphenyl)-1-butene,[46] 16.0 mg (4.1%); *trans*-3-methyl-1-(*p*-methoxyphenyl)-1-butene,[45] 5.3 mg (1.4%); 2-methyl-4-(*p*-methoxyphenyl)-2-butene,[47] 6.1 mg (1.6%); *tert*-butyl *p*-methoxybenzyl ether,[48] 22.6 mg (5.8%). The total volatile products were 282.4 mg (72.2%). The total mass balance was 391.3 mg (95.3%).

Exploratory Direct Photolysis of 1,1-Dimethyl-2-(*p*-methoxyphenyl)cyclopropane. Product Isolation and Identification. A solution of 192 mg of 1,1-dimethyl-2-(*p*-methoxyphenyl)cyclopropane[45] in 200 mL of *tert*-butyl alcohol was irradiated for 4.0 h (94% conversion). Analysis as described above of the photolyzate afforded 49.2 mg (26.7%) of nonvolatile material and the following: 1,1-dimethyl-2-(*p*-methoxyphenyl)cyclopropane,[45] 10.7 mg (5.8%); 2-methyl-4-(*p*-methoxyphenyl)-1-butene, 70.3 mg (38.2%); *cis*-3-methyl-1-(*p*-methoxyphenyl)-1-butene,[46] 12.4 mg (6.7%); *trans*-3-methyl-1-(*p*-methoxyphenyl)-1-butene,[46] 4.6 mg (2.5%); 2-methyl-4-(*p*-methoxyphenyl)-2-butene,[47] 4.6 mg (2.5%); *tert*-butyl *p*-methoxybenzyl ether,[48] 23.3 mg (12.7%). The total volatile products were 125.9 mg (68.4%). The total mass balance was 175.1 mg (95.2%).

Exploratory Direct Photolysis of 3-Methyl-3-(*m*-methoxyphenyl)-1-butene. Product Isolation and Identification. A solution of 506.0 mg of 3-methyl-3-(*m*-methoxyphenyl)-1-butene in 450 mL of *tert*-butyl alcohol was irradiated for 6.5 h (57.3% conversion). Analysis as described above of the photolyzate afforded 86.2 mg (17.9%) of nonvolatile material and the following: 3-methyl-3-(*m*-methoxyphenyl)-1-butene, 205.2 mg (42.7%); 1,1-dimethyl-2-(*m*-methoxyphenyl)cyclopropane, 108.3 mg (22.5%); 2-methyl-4-(*m*-methoxyphenyl)-1-butene,[49] 51.3 mg (10.7%); 2-methyl-4-(*m*-methoxyphenyl)-2-butene, 11.4 mg (2.4%); *tert*-butyl *m*-methoxybenzyl ether,[48] 5.5 mg (1.1%). The total volatile products were 381.7 mg (79.4%). The total mass balance was 467.9 mg (97.3%).

Exploratory Direct Photolysis of 1,1-Dimethyl-2-(*m*-methoxyphenyl)cyclopropane. Product Isolation and Identification. A solution of 429.9 mg of 1,1-dimethyl-2-(*m*-methoxyphenyl)cyclopropane in 450 mL of *tert*-butyl alcohol was irradiated for 7.8 h (64.1% conversion). Analysis as described above of the photolyzate afforded 83.6 mg (20.5%) of nonvolatile material and the following: 1,1-dimethyl-2-(*m*-methoxyphenyl)cyclopropane, 146.7 mg (35.9%); 2-methyl-4-(*m*-methoxyphenyl)-1-butene,[49] 109.4 mg (26.8%); 2-methyl-4-(*m*-methoxyphenyl)-2-butene, 40.9 mg (10.0%); *tert*-butyl *m*-methoxybenzyl ether,[48] 12.0 mg (2.9%). The total volatile products were 309.0 mg (75.7%). The total mass balance was 392.6 (96.1%).

Exploratory Direct Photolysis of 3-Methyl-3-(*p*-cyanophenyl)-1-butene. Product Isolation and Identification. A solution of 213.1 mg of 3-methyl-3-(*p*-cyanophenyl)-1-butene in 200 mL of *tert*-butyl alcohol was irradiated for 3 h (47.4% conversion). Analysis as described above of the photolyzate afforded 12.5 mg (6.1%) of nonvolatile material and the following: 3-methyl-3-(*p*-cyanophenyl)-1-butene, 107.7 mg (52.6%); 1,1-dimethyl-2-(*p*-cyanophenyl)cyclopropane, 59.7 mg (29.2%); 2-methyl-4-(*p*-cyanophenyl)-1-butene, 25.4 mg (12.4%); 2-methyl-4-(*p*-cyanophenyl)-2-butene, 2.1 mg (1.0%). The total volatile products were 194.9 mg (95.2%). The total mass balance was 201.5 mg (101.4%).

Exploratory Direct Photolysis of 1,1-Dimethyl-2-(*p*-cyanophenyl)cyclopropane. Product Isolation and Identification. A solution of 496.9 mg of 1,1-dimethyl-2-(*p*-cyanophenyl)cyclopropane in 450 mL of *tert*-butyl alcohol was irradiated for 6.5 h (42.4% conversion). Analysis as described above of the photolyzate afforded 43.5 mg (9.2%) of nonvolatile material and the following: 1,1-dimethyl-2-(*p*-cyanophenyl)cyclopropane, 271.9 mg (57.6%); 2-methyl-4-(*p*-cyanophenyl)-1-butene, 142.2 mg (30.1%); 2-methyl-4-(*p*-cyanophenyl)-2-butene, 11.8 mg (2.5%). The total volatile products were 425.9 mg (90.2%). The total mass balance was 469.7 mg (99.5%).

Exploratory Direct Photolysis of 3-Methyl-3-(*m*-cyanophenyl)-1-butene. Product Isolation and Identification. A solution of 205.9 mg of 3-methyl-3-(*m*-cyanophenyl)-1-butene in 200 mL of *tert*-butyl alcohol was irradiated for 1.0 h (43.3% conversion). Analysis as described of the photolyzate afforded 26.2 mg (13.3%) of nonvolatile material and the following: 3-methyl-3-(*m*-cyanophenyl)-1-butene, 112.15 mg (56.7%); 1,1-dimethyl-2-(*m*-cyanophenyl)cyclopropane, 17.21 mg (8.7%); 2-methyl-4-(*m*-cyanophenyl)-1-butene, 23.02 (11.6%); *cis*-3-methyl-1-(*m*-cyanophenyl)-1-butene, 4.60 mg (2.3%). The total volatile products were 156.7 mg (79.4%). The total mass balance was 176.5 mg (92.7%).

Exploratory Direct Photolysis of 1,1-Dimethyl-2-(*m*-cyanophenyl)cyclopropane. Product Isolation and Identification. A solution of 399.7 mg of 1,1-dimethyl-2-(*m*-cyanophenyl)cyclopropane in 400 mL of *tert*-butyl alcohol was irradiated for 1.0 h (60.1% conversion). Analysis as described above of the photolyzate afforded 66.2 mg (17.4%) of nonvolatile material and

---

[43] Wiley, R. H.; Smith, N. R. *J. Am. Chem. Soc.* **1948**, *70*, 1560–1561.

[44] Meites, L.; Meites, T. *Anal. Chem.* **1948**, *20*, 984–985.

[45] Moss, G. L.; Moss, R. A. *J. Am. Chem. Soc.* **1964**, *86*, 4042–4053.

[46] Schaarschmidt, A.; Georgeacopol, E.; Herzenberg *Chem. Ber.* **1918**, *51*, 1059–1074.

[47] Vdovtsova, E. A.; Yanichkin, L. R. *J. Org. Chem. USSR* **1969**, *5*, 933–939.

[48] Cristol, S. J.; Bindel, T. H. *J. Org. Chem.* **1980**, *45*, 951–957.

[49] Julia, M.; Labia, R. *Bull. Soc. Chim. Fr.* **1972**, 4151–4157.

Table XI. Direct Quantum Yield Photolyses of 3-Methyl-3-phenyl-1-butene

run	concn, mM	light abs[a]	% conv	photoprod, mmol	quantum yield
1	5.84	0.752	0.26	3.81×10^{-3}	0.00507
2	5.76	0.726	0.27	3.87×10^{-3}	0.00533
3	5.92	1.096	0.38	5.61×10^{-3}	0.00513
4	5.56	1.322	0.45	6.24×10^{-3}	0.00472

[a] In units of millieinsteins.

Table XII. Direct Quantum Yield Photolyses of 3-Methyl-3-(*p*-methoxyphenyl)-1-butene

run	concn, mM	light abs[a]	% conv	photoprod, mmol	quantum yield
1	3.59	0.179	1.07	8.81×10^{-3}	0.0491
2	3.36	0.161	1.11	8.29×10^{-3}	0.0513
3	3.37	0.240	1.65	1.28×10^{-2}	0.0493
4	3.34	1.73	5.51	4.60×10^{-2}	0.0467

[a] In units of millieinsteins.

the following: 1,1-dimethyl-2-(*m*-cyanophenyl)cyclopropane, 151.4 mg (39.9%); 2-methyl-4-(*m*-cyanophenyl)-1-butene, 109.4 mg (28.8%); *cis*-3-methyl-1-(*m*-cyanophenyl)-1-butene, 33.8 mg (8.9%). The total volatile products were 294.6 mg (77.6%). The total mass balance was 358.9 mg (94.5%).

Exploratory Sensitized Photolysis of 3-Methyl-3-(*p*-cyanophenyl)-1-butene. Product Isolation and Identification. A solution of 104.2 mg of 3-methyl-3-(*p*-cyanophenyl)-1-butene in 250 mL of acetone was photolyzed for 2.2 h and 4.3 meinsteins absorbed (57.8% conversion). Analysis of the photolyzate as described above afforded the following: 3-methyl-3-(*p*-cyanophenyl)-1-butene, 44.0 mg (42.2%); 1,1-dimethyl-2-(*p*-cyanophenyl)cyclopropane, 57.6 mg (55.3%). The total mass balance was 101.6 mg (97.5%).

Exploratory Sensitized Photolysis of 3-Methyl-3-(*m*-cyanophenyl)-1-butene. Product Isolation and Identification. A solution of 106.3 mg of 3-methyl-3-(*m*-cyanophenyl)-1-butene in 240 mL of acetone was irradiated for 2.0 h and 3.9 meinsteins absorbed (49.8% conversion). Analysis of the photolyzate as described above afforded 3-methyl-3-(*m*-cyanophenyl)-1-butene, 53.4 mg (50.2%), and 1,1-dimethyl-2-(*m*-cyanophenyl)cyclopropane, 50.5 mg (48.5%). The total mass balance was 103.9 mg (97.8%).

Photolysis Apparatus for Quantum Yield Determinations. Quantum yield determinations were performed by using the black box apparatus[50] or a semimicrooptical bench.[50] Light output for each run was measured by using a digital actinometer[51] calibrated by ferrioxalate actinometry.[52] Microoptical bench photolysis employed an Osram HBO 200-W high-pressure mercury lamp and Bausch and Lomb Model 33-86-79 monochromator with a 5.4-mm entrance slit and 3.0-mm exit slit, giving a band pass of 22 nm at half-peak height. The band pass for the black box was controlled by the filter solution combinations held in a 750-mL total volume three-compartment quartz-faced filter solution cell. The filter solution combinations were as follows: filter A (cell 1, 2.00 M nickel sulfate in 5% sulfuric acid; cell 2, 0.80 M cobalt sulfate in 5% sulfuric acid; cell 3, 2.5×10^{-4} M bismuth trichloride in 15% hydrochloric acid; transmission, 0% below 250 nm, 37.5% at 286 nm, 0% above 310 nm); filter B (cell 1, 2.00 M nickel sulfate in 5% sulfuric acid; cell 2, 0.80 M cobalt sulfate in 5% sulfuric acid; cell 3, 0.0090 M 2,7-dimethyl-3,6-diazacyclohepta-1,6-diene perchlorate[53] in water; transmission, 0% below 237 nm, 5% at 254 nm, 0% above 265 nm). Direct photolyses were run in purified cyclohexane[54] purged with deoxygenated nitrogen[44] for 1 h before each run. Analysis was by vapor phase chromatography on Column A with naphthalene as an internal standard.

Table XIII. Direct Quantum Yield Photolyses of 3-Methyl-3-(*m*-methoxyphenyl)-1-butene

run	concn, mM	light abs[a]	% conv	photoprod, mmol	quantum yield
1	4.69	0.341	1.68	1.97×10^{-2}	0.0577
2	4.53	1.21	5.47	6.18×10^{-2}	0.0511
3	4.65	1.89	8.10	9.42×10^{-2}	0.0499

[a] In units of millieinsteins.

Table XIV. Direct Quantum Yield Photolyses of 3-Methyl-3-(*p*-cyanophenyl)-1-butene

run	concn, mM	light abs[a]	% conv	photoprod, mmol	quantum yield
1	2.19	0.441	10.8	5.90×10^{-2}	0.134
2	2.20	0.482	11.0	5.71×10^{-2}	0.118
3	2.21	0.908	16.4	8.90×10^{-2}	0.0981

[a] In units of millieinsteins

Table XV. Direct Quantum Yield Photolyses of 3-Methyl-3-(*m*-cyanophenyl)-1-butene

run	concn, mM	light abs[a]	% conv	photoprod, mmol	quantum yield
1	4.13	0.342	1.94	2.00×10^{-2}	0.0586
2	3.82	0.508	2.99	2.86×10^{-2}	0.0562
3	3.76	1.28	6.61	6.01×10^{-2}	0.0468

[a] In units of millieinsteins.

Table XVI. Quenched Direct Quantum Yield Photolyses of 3-Methyl-3-(*p*-methoxyphenyl)-1-butene

run	concn, mM	quencher concn, mM	light abs[a]	% conv	photoprod, mmol	quantum yield
1	3.57	3.00	0.200	0.87	7.73×10^{-3}	0.0386
2	3.58	3.00	0.179	0.72	6.50×10^{-3}	0.0363

[a] In units of millieinsteins.

Table XVII. Quenched Direct Quantum Yield Photolyses of 3-Methyl-3-(*m*-methoxyphenyl)-1-butene

run	concn, mM	quencher concn, mM	light abs[a]	% conv	photoprod, mmol	quantum yield
1	2.44	0.83	0.117	0.82	5.01×10^{-3}	0.0427
2	2.58	0.85	0.190	1.12	7.26×10^{-3}	0.0382

[a] In units of millieinsteins.

Table XVIII. Acetone Sensitized Quantum Yield Photolyses

compd	run	concn, mM	light abs[a]	% conv	photoprod, mmol	quantum yield
p-CN	1	4.17	0.0115	4.07	7.30×10^{-3}	0.705
p-CN	2	4.10	0.00332	1.17	2.06×10^{-3}	0.711
m-CN	1	4.11	0.0101	1.28	2.26×10^{-3}	0.249

[a] In units of millieinsteins.

Direct Quantum Yield Results. 3-Methyl-3-phenyl-1-butene[55] was photolyzed through filter solution B. All other 3-methyl-3-aryl-1-butenes were photolyzed through filter solution A. Results are reported in Tables XI–XV.

Quenched direct runs used filter solution A. The quencher was biacetyl (see below for purification). Results are reported in Tables XVI and XVII.

Sensitized Quantum Yield Results. Runs were in acetone (MCB, Reagent ACS) with the semimicrooptical bench at 300 nm. Results are reported in Table XVIII.

Measurement of Triplet Parameters. The general method of Sandros[10e] for determining the rate of intersystem crossing and

---

[50] Zimmerman, H. E. *Mol. Photochem.* **1971**, *3*, 281–292.

[51] Zimmerman, H. E.; Cutler, T. P.; Fitzgerald, V. R.; Weight, T. J. *Mol. Photochem.* **1977**, *8*, 379–385.

[52] Hatchard, C. C.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518.

[53] Schwartzenbach, G.; Lutz, K. *Helv. Chim. Acta* **1940**, *23*, 1139.

[54] Zimmerman, H. E.; Kreil, D. J. *J. Org. Chem.* **1982**, *47*, 2060–2075.

[55] Hiyama, T.; Yamamoto, H.; Nishio, K.; Kitatani, K.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3632–3637.

Table XIX. Biacetyl Emission Data for 3-Methyl-3-phenyl-1-butene

no.	compd concn, mM	biac concn, mM	420 nm excit		260 nm excit		R
			fluor	phos	fluor	phos	
1	73.5	0.668	0.468	2.22	0.177	0.831	0.990
2	73.5	1.07	0.361	1.96	0.206	1.11	1.00
3	73.5	1.34	0.943	4.80	0.308	1.60	1.02
4	73.5	1.61	0.529	4.33	0.256	2.10	1.01
5	73.5	2.13	0.695	4.16	0.395	2.25	0.952

Table XX. Biacetyl Emission Data for 3-Methyl-3-(*p*-cyanophenyl)-1-butene

no.	compd concn, mM	biac concn, mM	420 nm excit		270 nm excit		R
			fluor	phos	fluor	phos	
1	3.29	0.283	0.561	6.92	0.111	1.43	1.04
2	3.29	0.566	1.09	13.4	0.225	2.89	1.05
3	6.58	1.09	0.376	3.96	0.386	4.24	1.04
4	6.58	3.28	0.989	10.2	0.950	9.43	0.962

Table XXI. Biacetyl Emission Data for 3-Methyl-3-(*m*-cyanophenyl)-1-butene

no.	compd concn, mM	biac concn, mM	420 nm excit		270 nm excit		R
			fluor	phos	fluor	phos	
1	2.10	0.506	0.960	13.3	0.177	2.32	1.05
2	2.63	0.697	1.32	13.5	0.167	1.69	0.994
3	2.10	1.01	1.91	22.1	0.380	4.62	0.953
4	2.63	1.39	2.30	18.9	0.316	2.50	1.04

Table XXII. Biacetyl Emission Data for 3-Methyl-3-(*p*-methoxyphenyl)-1-butene

no.	compd concn, mM	biac concn, mM	420 nm excit		270 nm excit		R
			fluor	phos	fluor	phos	
1	1.0	0.407	0.972	4.95	0.225	1.28	1.12
2	1.0	0.453	1.14	6.62	0.332	1.92	0.99
3	2.0	0.748	0.271	4.00	0.180	3.21	1.21
4	2.0	0.813	1.99	8.88	0.123	0.974	1.72
5	1.0	0.906	2.15	13.1	0.517	3.66	1.16
6	2.0	0.995	0.370	5.40	0.315	5.38	1.17
7	2.0	1.50	0.521	7.26	0.402	6.58	1.17
8	2.0	1.18	0.629	6.71	0.601	6.69	1.04
9	2.0	2.98	1.04	11.7	0.838	10.6	1.12
10	2.0	3.62	1.20	15.3	0.872	12.5	1.12

Table XXIII. Biacetyl Emission Data for 3-Methyl-3-(*m*-methoxyphenyl)-1-butene

no.	compd concn, mM	biac concn, mM	420 nm excit		270 nm excit		sandros function
			fluor	phos	fluor	phos	
1	2.34	1.60	0.577	7.95	0.154	2.76	3.36
2	2.34	1.97	0.599	8.85	0.149	2.79	3.75
3	2.34	2.21	0.653	9.86	0.199	3.73	4.12
4	2.34	3.95	1.24	15.4	0.357	5.07	6.90
5	2.34	4.41	1.24	15.3	0.404	5.64	7.90

the triplet lifetime of benzenoid compounds by sensitized biacetyl phosphorescence and fluorescence was used.

All 3-methyl-3-aryl-1-butenes were purified by vapor phase chromatography on column B. Biacetyl (Aldrich) was purified by drying over magnesium sulfate, distillation in vacuo twice, and fractional freezing three times. The biacetyl was protected from light and stored at 0 °C. The solvent was methylcyclohexane (Kodak Spectro Grade).

For each compound, a series of samples in methylcyclohexane was prepared with compound optical density of 3–4 and biacetyl concentration of 0.0005–0.004 M. The samples were throughly degassed by standard freeze–pump–thaw technique with the last thaw under oxygen-free nitrogen. Biacetyl fluorescence (460 nm) and phosphorescence (510 nm) were monitored in an Aminco-Bowman spectrofluorimeter by an RCA 4818 photomultiplier, through a plate of Corning 3-75 filter glass which excluded the second order of the excitation light (260–270 nm). Irradiation of the sample at 420 nm was through a Corning 0-52 filter glass to exclude stray light at short wavelength. The Corning 0-52 filter was removed for sample irradiation at 260–270 nm depending on the compound.

Biacetyl fluorescence and phosphorescence intensities were measured (arbitrary units) first with the sample irradiated at 420 nm where only biacetyl absorbed and then with the sample irradiated in the range 260–270 nm. The phosphorescence intensity was corrected for fluorescence present at 510 nm by subtracting 0.249 times the fluorescence intensity (460 nm) from the phosphorescence intensity (510 nm).[10e] Biacetyl absorbed less than 2% of the light when the sample was irradiated in the 260–270 nm range. R is the ratio $[(P/F)_{270}/(P/F)_{420}]$.

Summary of Results for Triplet Parameters. Biacetyl emission data for 3-methyl-3-phenyl-1-butene,[55] 3-methyl-3-(*p*-cyanophenyl)-1-butene, and 3-methyl-3-(*m*-cyanophenyl)-1-butene are shown in Tables XIX–XXI. Biacetyl emission data for 3-methyl-3-(*p*-methoxyphenyl)-1-butene and 3-methyl-3-(*m*-methoxyphenyl)-1-butene are reported in Tables XXII and XXIII. Plotting the data for 3-methyl-3-(*m*-methoxyphenyl)-1-butene (see Table XXIII) using the Sandros function[10e] yielded the following results: correlation coefficient (r^2), 0.996; Y intercept, 0.619; slope, 1.62×10^3; k_{isc}, 9.25×10^6 s^{-1}; k_{dtot}, 5.73×10^6 s^{-1}; $^3\tau$, 175 ns. Quenching rate constants were taken from Sandros,[10e] $k_q = 1.5 \times 10^{10}$ s^{-1}.

Single Photon Counting. The apparatus and procedure have been described previously.[8b] Solvents were methylcyclohexane (Kodak Spectro Grade) and isopentane purified as described previously.[8b]. Individual samples were prepared in a 4:1 methylcyclohexane–isopentane solution to give an optical density in the range 0.80–2.3, thoroughly degassed immediately before counting and counted at 21 °C until a minimum of 2000 counts in the maximum channel (512 channels total) was obtained. Data were collected at less than 5% of lamp flash frequency to ensure exclusion of double photon counting. In separate runs excitation was varied over the range 250–280 nm and emission was monitored over the range 295–320 nm with an RCA 8850 photomultiplier. The decay range was independent of excitation wavelength, emission wavelength, and optical density to within 5%. The data are reported as follows: compound, average lifetime, average decay rate, number of runs, average A value.

(1) 3-Methyl-3-phenyl-1-butene, 9.18 ns, $1.09 \times 10^8\ s^{-1}$, 3, 0.028.

(2) 3-Methyl-3-(*p*-methoxyphenyl)-1-butene, 4.38 ns, $2.28 \times 10^8\ s^{-1}$, 3, 0.040.

(3) 3-Methyl-3-(*m*-methoxyphenyl)-1-butene, 4.60 ns, $2.18 \times 10^8\ s^{-1}$, 3, 0.040.

(4) 3-Methyl-3-(*p*-cyanophenyl)-1-butene, 10.3 ns, $9.67 \times 10^7\ s^{-1}$, 3, 0.027.

(5) 3-Methyl-3-(*m*-cyanophenyl)-1-butene, 4.88 ns, $2.05 \times 10^8\ s^{-1}$, 2, 0.035.

Calculations. The general Pople semiempirical SCF approach[56] (ZDO) was used. A CI treatment was applied to the SCF MOs including both single and double excitations. For both single and double excitations all orbitals were included. Configurations were selected by a first-order perturbation approach.[57] Configurations were represented as a linear combination of Slater determinants such that each configuration was an eigenfunction of the spin operator S^2 as described by Murrell and McEwen.[58] Matrix elements between configurations were calculated from general formulas obtained by the standard methods for reduction of many-electron integrals.[56,58]

Valence-state ionization potentials were those described by Hinze and Jaffe.[59] Two-electron repulsion integrals were calculated by the Pariser–Parr approach.[60] Resonance integrals were calculated by the expression $\beta_{ij} = (S_{ij}/(1 + S_{ij}))(I_i + I_j)K$ where S_{ij} is the overlap integral[61] and I_i and I_j are the valence-state ionization potentials for orbitals i and j, respectively. Nearest-neighbor and selected 1,3-resonance integrals were used. The constant K was obtained by fitting β to the spectral transition of ethylene with a configuration interaction calculation that included single and double excitations.[57a]

Standard geometries were assumed, based on reported model compounds.[62] Geometries of intermediate species were assumed.

Calculations were performed with Fortran IV programs[57a] on a PDP-11/T55 computer having 32K words of memory. Direct access to and from two disks of 1.2×10^6 words per disk allowed storage and use of the large matrices encountered in configuration interaction calculations.

Acknowledgment. Support of this research by the National Science Foundation and by the National Institutes of Health Grant GM07487 is gratefully acknowledged. The synthetic portions of this research were supported by NIH while the theoretical and quantitative aspects were supported by NSF.

Registry No. 3, 18321-36-3; **4a**, 18272-88-3; **4b**, 84565-67-3; **5a**, 90433-15-1; **5b**, 90433-16-2; **7a**, 90433-31-1; **7b**, 90433-21-9; **8a**, 90433-23-1; **8b**, 90433-24-2; **9a**, 18491-21-9; **10a**, 90433-26-4; **10b**, 90433-28-6; **11b**, 18272-91-8; **12**, 90433-29-7; **14**, 90433-30-0; **18**, 90433-20-8; **19a**, 32454-14-1; **19b**, 32454-15-2; **19c**, 32454-16-3; **19d**, 90433-17-3; **20a**, 90433-18-4; **20b**, 90433-19-5; **23**, 932-77-4; **24a**, 90433-22-0; **24b**, 90433-25-3; **25**, 3506-70-5; **26**, 90433-27-5; **27**, 104-20-1; **28**, 30780-21-3; **29**, 65292-99-1; **30**, 27200-79-9; **31**, 85964-37-0; **32**, 24964-64-5; **37**, 90460-09-6; **38**, 90460-07-4; **39**, 90433-32-2; **40**, 90433-33-3; **41**, 90460-08-5; triphenylphosphonium bromide, 1779-49-3; ethyl acetoacetate, 141-97-9; isopropyltriphenylphosphonium iodide, 1530-33-2; (2-methylpropyl)triphenylphosphonium bromide, 22884-29-3.

---

(56) (a) Zimmerman, H. E. "Quantum Mechanics for Organic Chemist"; Academic Press: New York, 1975. (b) Dewar, M. J. S. "The Molecular Orbital Theory of Organic Chemistry"; McGraw-Hill: New York, 1969.

(57) (a) Zimmerman, H. E.; Steinmetz, M. G., unpublished results. (b) Buenker, R. J.; Peyerimhoff, S. D. *Theor. Chim. Acta* **1974**, *35*, 33–58.

(58) Murrell, J. N.; McEwen, K. L. *J. Chem. Phys.* **1956**, *25*, 1143–1149.

(59) Hinze, J.; Jaffe, H. H. *J. Am. Chem. Soc.* **1962**, *84*, 540–546.

(60) Pariser, R.; Parr, R. G. *J. Chem. Phys.* **1953**, *21*, 767–776.

(61) Mulliken, R. S.; Rieke, C. A.; Orloff, D.; Orloff, H. *J. Chem. Phys.* **1949**, *17*, 1248–1267.

(62) Kennard, O., Ed. "Molecular Structures and Dimensions"; Unwin Brothers: Cambridge, England, 1972; Vol. A1.

Kinetic and Stereochemical Study on Bimolecular Substitution Reactions of Hydrazonates, Thiohydrazonates, and Hydrazonoyl Chlorides with Methoxide Ion

Jeffrey E. Rowe[1a] and Anthony F. Hegarty*[1b]

Organic Chemistry Department, La Trobe University, Bundoora, Victoria 3083, Australia, and Chemistry Department, University College, Belfield, Dublin 4, Ireland

Received January 5, 1984

Reaction of the (*Z*)-hydrazonoyl chlorides **2** with methoxide ion in methanol, under conditions where kinetic results show the reaction is bimolecular, leads to stereospecific formation of the (*Z*)-methyl hydrazonates, **5**. Less than 2% of the product with the "inverted" configuration at carbon (**6**) is formed. When a poorer leaving group than Cl^- is involved, then mixtures of *E* and *Z* products result. Thus the aryl thiohydrazonates (**3**) which have the *Z* configuration give 84–90% of the (*Z*)-methyl hydrazonate on reaction with methoxide ion. The (*E*)-aryl hydrazonates undergo reaction ca. 12-fold more slowly and isomer ratios of the (*Z*)- and (*E*)-methyl hydrazonates which result are closer to 1:1. The product methyl hydrazonates **5** and **6** undergo MeO^--catalyzed interconversion to an equilibrium mixture which favors **6**, but at a slower rate than the formation of either **5** or **6**. The stereochemical outcome of these displacements at the C═N bond is rationalized in terms of stereoelectronic control of the addition and elimination steps.

Introduction

Two general mechanisms for nucleophilic substitution at the carbon nitrogen doublet bond have been identified (Scheme I).

The ionization pathway (i) dominates the chemistry of imidoyl halides[2] owing to the stabilization of the nitrilium ion formed by the adjacent lone pair. We have shown previously[3] that the product is formed by this route

---

[1] (a) La Trobe University. (b) University College Dublin.

[2] Hegarty, A. F.; Cronin, J. D.; Scott, F. L. *J. Chem. Soc., Perkin Trans. 2*, **1975**, 429.