

A Ranking of Diylphilic Reactivities of Olefins toward the Singlet and Triplet Forms of the Trimethylenemethane Biradical, 2-Isopropylidenecyclopenta-1,3-diyl

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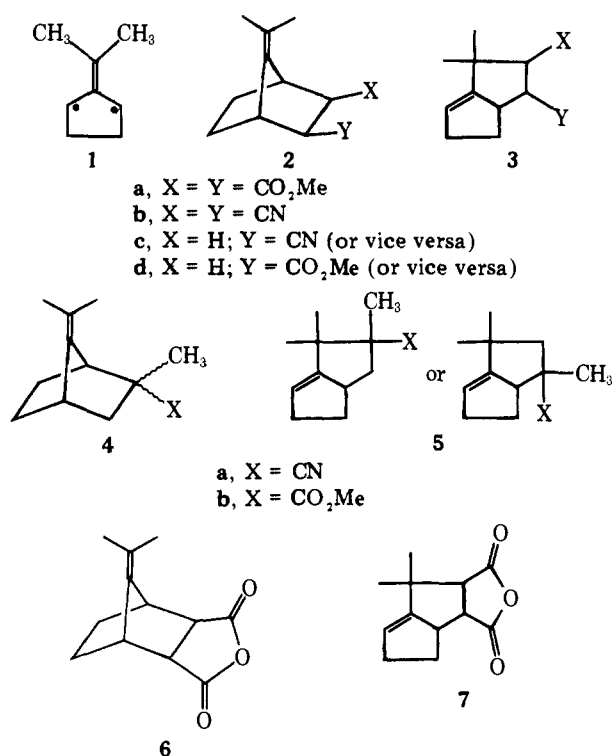
Abstract: The relative rates of cycloaddition of olefins with the trimethylenemethane (TMM) derivative 2-isopropylidenecyclopenta-1,3-diyl (**1**) can be determined by direct competition experiments. The gross relative activities in turn can be dissected into singlet and triplet relative reactivities by two techniques. The first involves the determination of the competition ratio for entrapment of the singlet TMM by a given olefin vs. intersystem crossing (isc) to the triplet, combined with the assumption that the rate of isc is independent of the olefin. The second uses the concentration of a "marker" product from the limiting singlet product distribution (obtained from oxygen-saturated runs) and the limiting spin-equilibrated (mostly triplet) product distribution as a guide to the fraction of singlet-derived and triplet-derived products from a given olefin under the conditions of competition. The relative reactivities toward the singlet follow: maleic anhydride, 235; maleonitrile, 180; fumaronitrile, 160; dimethyl fumarate, 67; acrylonitrile, 4.5; methyl acrylate, 0.9; dimethyl maleate, 1.0. The relative triplet reactivities for the last four olefins are respectively 59, 35, 12, and (1.0). The results are consistent with the idea of a concerted cycloaddition of the singlet and a nonconcerted one of the triplet.

The cycloaddition of 2-isopropylidenecyclopenta-1,3-diyl (**1**) to conjugated olefins is a general reaction in which a new methylenecyclopentane moiety is formed.^{2,3} Previous work^{2,4a} shows that it is possible to observe reactions of both a singlet (S)⁵ and a triplet (T) state of the diyl. We report here^{4b} a quantitative ranking of the relative reactivities of a series of seven olefins toward the singlet and four of the same olefins toward the triplet. The triplet and singlet reactivities are determined by direct competition experiments, and the singlet reactivity scale is checked by an independent technique which relies upon the previously described^{2,4} dilution effect. The next section describes the identification of the cycloadducts of the olefins. Readers to whom these details are of secondary interest may resume the mechanistic analysis in the section headed "Relative Singlet Reactivities from the Dilution Effect".

Identification of the Cycloadducts. The structures and configurations of the bridged and fused cycloadducts of dimethyl maleate, dimethyl fumarate, and maleic anhydride (**2a**, **3a**, **6**, and **7**) with diyl **1** have been described elsewhere.² The remaining bridged adducts **2** and **4** are identified by comparison of gas chromatographic (GC) retention times and/or nuclear magnetic resonance (NMR) spectra with those of independently synthesized materials. The latter are obtained by a sequence initiated by Diels-Alder addition of 6,6-dimethylfulvene to the olefin followed by semihydrogenation. The fused adducts **3** and **5** are identified by mass spectrometry, which establishes them as 1:1 adducts of **1** and olefin, and, in most cases, by NMR spectroscopy. Table I summarizes the bases for the assignments, which are described in more detail in the Experimental Section.

Relative Singlet Reactivities from the Dilution Effect. The cascade mechanism for the formation of cycloadducts from the decomposition of the diazene **8** is shown in Scheme I. If we assume that the intersystem crossing rate constant, k_5 , is independent of the nature of the trapping olefin, the ratio $(k_1 + k_2)/k_5$ for any olefin would be a measure of its reactivity toward the singlet diyl. In this section, we analyze the adduct distribution as a function of concentration in order to obtain $(k_1 + k_2)/k_5$ for methyl acrylate, acrylonitrile, and dimethyl maleate, using methods similar to those previously applied² in the case of dimethyl fumarate.

Methyl Acrylate and Acrylonitrile. Three fused (F_1 , F_2 , F_3) and two bridged (B_1 and B_2) isomers are formed in the thermal decomposition of diazene **8** in the presence of a large excess of methyl acrylate in acetonitrile as solvent. Although the detailed



structures of the fused products **3d** are unknown, the appearance of *three* isomers in similar amounts means that orientation of the lone substituent within the fused series is not highly specific.

The limiting singlet and spin-equilibrated (mostly triplet) product distributions (Table II) are obtained from pyrolyses in the presence of oxygen and from high-dilution runs, re-

Scheme I

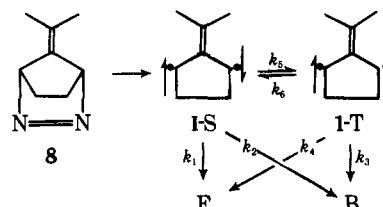


Table I. Bases^a for the Structural and Stereochemical Assignments to Adducts of Diyl **1** and Olefins

olefin	bridged adducts		fused adducts	
	GC	isol, NMR	MS	isol, NMR
maleic anhydride ^b	X		X	X
<i>trans</i> -NCCH=CHCN	X		X	X
<i>cis</i> -NCCH=CHCN	X		X	X
<i>trans</i> -MeO ₂ CCH=CH-CO ₂ Me ^b	X	X	X	X
CH ₂ =C(Me)CN	X		X	
CH ₂ =CHCN	X	X	X	X
CH ₂ =CHCO ₂ Me	X	X	X	X
CH ₂ =C(Me)CO ₂ Me	X		X	
<i>cis</i> -MeO ₂ CCH=CH-CO ₂ Me ^b	X	X	X	X

^a A symbol X appears where this technique was applied. ^b Reference 2.

spectively. Corresponding results are given for acrylonitrile, from data obtained in the present work, and for dimethyl maleate and dimethyl fumarate, from the previous work.² The fractions X_S and $X_T (= 1 - X_S)$ of singlet- and triplet-derived products at any given concentration of trapping agent [N] may be calculated from the observed fraction of the *i*th product (I_{obsd}) from eq 1, where I_S and I_T are the fractions of the *i*th product in the limiting singlet and triplet product distributions (Table II). These distributions are best determined by monitoring one or more products whose concentrations change markedly with dilution.

$$I_{\text{obsd}} = I_S X_S + I_T (1 - X_S) \quad (1)$$

The relationship between the singlet-triplet product ratio, the concentration of trapping agent, and the various rate constants of Scheme 1 is given by eq 2.² A plot of X_S/X_T should be linear with a slope that may be equated directly with the desired ratio, $(k_1 + k_2)/k_5$.

$$X_S/X_T = \frac{k_6(k_1 + k_2)}{k_5(k_3 + k_4)} + \frac{(k_1 + k_2)[N]}{k_5} \quad (2)$$

Figures 1 and 2 show these plots for methyl acrylate and acrylonitrile ($r = 0.997$ in each case). Both graphs show intercepts near zero. In the acrylonitrile case, the small negative value (-0.15) has no physical significance in terms of eq 2 and presumably should be interpreted as within experimental error of zero. It should be noted that a near-zero intercept would be expected (eq 2) if the equilibrium constant (k_5/k_6 , Scheme 1) favoring the ground-state triplet over the singlet diyl⁹ is large enough to overbalance any kinetic preference for capture of the singlet.

The linear regression slopes of Figures 1 and 2 give values (in L mol⁻¹) of 0.34 (methyl acrylate) and 0.89 (acrylonitrile), respectively, for $(k_1 + k_2)/k_5$.

Dimethyl Maleate. The adducts in this system are the ste-

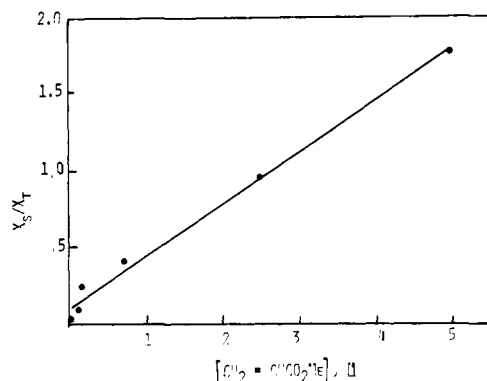


Figure 1. Linear regression of the ratio of singlet and triplet derived products as a function of concentration in the reaction of methyl acrylate with **1** at 60 °C in CH₃CN solvent. The slope measures $(k_1 + k_2)/k_5$ (Scheme 1) and has the value 0.34 L mol⁻¹ for methyl acrylate.

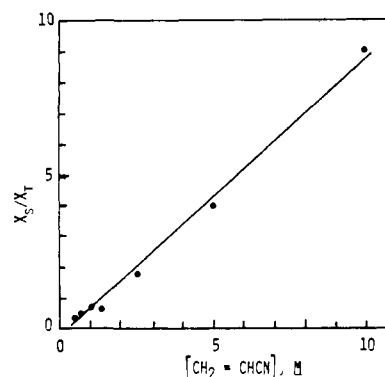


Figure 2. Same as Figure 1 but for acrylonitrile. The slope is 0.89 L mol⁻¹.

reoisomers of **2a** and **3a**. Following the previous nomenclature,² we use a lower-case letter (*c* or *t*) to indicate the configurational relationship of X and Y, an upper-case letter (B or F) to indicate a bridged or fused structure, and a subscript number to indicate the order of emergence from GC of the members of a group. The data require a slightly different analysis from that given above because, as the previous study² shows, even in neat, oxygenated dimethyl maleate as solvent, the true limiting singlet product distribution is not achieved. Also the low reactivity of dimethyl maleate permits some of the diyl to elude capture and appear as diyl dimer. Moreover, there is an experimental difficulty in that the GC analysis fails to resolve two of the adduct components, *t*F₂ and *c*F₁. It seems unlikely² that *t*F₂ is a singlet product from maleate, but we find that, even if it is assumed to be, the conclusions are not seriously affected.

It is a reasonable assumption² that the total *cis*-fused cycloadduct is a measure of singlet product in the maleate system.

Table II. Limiting Singlet and Spin-Equilibrated Product Distributions in the Reactions of Diyl **1** with Olefins (X = CO₂Me)

olefin	distribn	adduct, %					F/B
		F ₁	F ₂	F ₃	B ₁	B ₂	
CH ₂ =CHX ^c	<i>I</i> _S ^a	8.5	60	31	1	0.5 ^h	~80
	<i>I</i> _T ^b	3.2	66	4	15	14 ^h	
CH ₂ =CHCN ^c	<i>I</i> _S ^a	29	36	32 ^g	3 ^h		31
	<i>I</i> _T ^b	41	28	3 ^g	27 ^h		
<i>cis</i> -XCH=CHX ^d	<i>I</i> _S	2 ^h	41 ^e	55 ^g	1 ^h	1	~8
	<i>I</i> _T	24 ^h	14 ^e	6 ^g	53 ^h	6	
<i>trans</i> -XCH=CHX ^d	<i>I</i> _S	56	43 ^{e,g}	~0	1.3 ^{f,h}	~0	~8
	<i>I</i> _T	36	10 ^{e,g}	~0	46 ^{f,h}	~8	

^a Determined on oxygenated solutions. ^b Values extrapolated to "infinite" dilution. ^c Present work. ^d Reference 2. ^e *t*F₂ + *c*F₁. ^f *t*B. ^g Used to calculate *F*_S. ^h Used to calculate *F*_T.

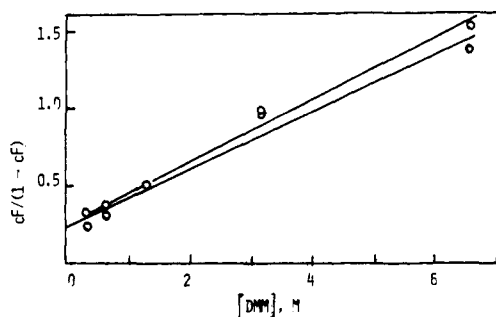


Figure 3. Ratio of cis-fused to all other products as a function of olefin concentration in the pyrolysis of **8** with dimethyl maleate (DMM) in CH₃CN at 60 °C. The two curves are derived from two alternative assumptions (see text). The slopes are 0.17 and 0.16 L mol⁻¹.

If we plot the ratio of cis-fused to all *other* products, including diyl dimers, vs. dimethyl maleate concentration, we should obtain a plot that bears the same relationship to eq 2 as those of Figures 1 and 2. Figure 3 shows two such plots based upon the limiting assumptions that the unresolved VPC peak is either all *cF*₁ or all *tF*₂. The slopes in L mol⁻¹ are 0.17 and 0.16.

The ratios of singlet capture vs. intersystem crossing for the three systems of Figures 1-3 are combined with the previously determined² dimethyl fumarate value $(k_1 + k_2)/k_S = 7.7$ L mol⁻¹ to give the relative singlet reactivities shown in Table III.¹⁰

Relative Reactivities of Olefins toward the Singlet and Triplet Diyls by Competition Experiments. The rank-order of singlet reactivities found in Table III can be confirmed by direct competition experiments, which also form the basis for a ranking of olefins toward the triplet diyl 1-T. Because the competition experiments may be performed more quickly, it is practical to develop a more extensive set of data and thereby to develop a qualitative theory of diyl-olefin reactivity.

The relative reactivities are determined by observation of the competition between pairs of olefins in forming adducts from diyl 1, which is generated in thermal decomposition at ~60 °C of diazene **8**. The initial ratio of olefin to diazene is 8-10, and the total olefin concentration is 1-2 M. The reactions are carried out in carefully degassed acetonitrile solution containing 2-methoxynaphthalene as internal standard. Calibration of the flame ionization detector response for gas chromatographic (GC) analysis is achieved using gravimetrically prepared known solutions of internal standard and adducts of the bridged series, prepared by semihydrogenation of adducts from the Diels-Alder reaction of the appropriate olefin and 6,6-dimethylfulvene.

The products from the decompositions of diazene **8** are shown to be 1:1 adducts of diyl 1 and olefin by GC-mass spectrometry. In most cases, the adducts account for >95% of the diazene reacted.

The gross relative reactivities are derived from eq 3, where

$$R_i/R_j = (P_i/P_j) (C_j/C_i) \quad (3)$$

R_i/R_j is the reactivity of olefin *i* relative to that of olefin *j* toward the diyl, P_i/P_j is the product ratio, and C_j/C_i is the initial ratio of olefin concentrations. This treatment assumes that the kinetic order in the diyl + olefin reaction is the same for all the olefins studied and that the ratio of olefin concentrations remains unchanged during reaction. The first assumption cannot yet be proven but is reasonable. The second is assured by the use of a large excess of olefin and by the experimental demonstration⁴ that dimethyl maleate and dimethyl fumarate, cis-trans isomeric olefins, do not interconvert under the reaction conditions.

Because each olefin forms adducts derived from both the

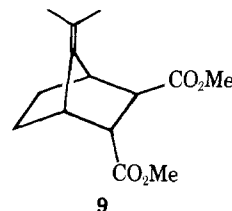
Table III. Relative Reactivities of Olefins in Capturing Singlet Diyl 1 Based upon Dilution Studies

olefin	rel react to 1-S
<i>cis</i> -MeO ₂ CCH=CHCO ₂ Me	(1.0)
CH ₂ =CHCO ₂ Me	1.2
CH ₂ =CHCN	3.2
<i>trans</i> -MeO ₂ CCH=CHCO ₂ Me	48

singlet and the triplet forms of the diyl, the gross relative reactivities are weighted averages of the individual singlet and triplet reactivities. These can be dissected by an application of the dilution technique describe above and elsewhere.^{2,4}

In principle, the measured gross or composite relative reactivity R_i is a function of the individual singlet and triplet reactivities and the contribution that each spin state makes to the product, expressed as F_S and F_T , the percents of product from singlet and triplet. The terms F_S and F_T may be evaluated for each olefin under each set of competition conditions by an examination of the distribution of products from each, provided, of course, that the competing olefins, *i* and *j*, are not stereoisomers and hence do not give any products in common. In our series, the only pair that does not meet this criterion is the maleate-fumarate system, for which a special analysis will be described later.

For the other cases, we may use the concentration of a "marker" product from the limiting singlet reaction (high olefin concentration, oxygen saturated) and from the limiting spin-equilibrated (mostly triplet) reaction as a guide to F_S and F_T under intermediate conditions. For example, the reaction of dimethyl fumarate with the singlet diyl gives an adduct mixture containing 1.3% of the trans-bridged (*tB*) product **9**,



whereas this product forms 46% of the adduct mixture from the triplet diyl² (Table II). In a competition experiment, if we may make the reasonable assumption that the presence of the second olefin does not change the limiting product distribution characteristic of dimethyl fumarate, we may use the same formula (eq 4) as before² to calculate F_T .

$$F_T = 100(\% tB_{\text{obsd}} - 1.3)/(46 - 1.3) \quad (4)$$

An independent check on this procedure in the fumarate system comes from an examination of a second "marker" product, *tF*₂, which accounts for 43% of the singlet distribution but only 10% of the triplet distribution.² From this, we obtain

$$F_S = 100(\% tF_{\text{obsd}} - 10)/(43 - 10) \quad (5)$$

Since the two-intermediate mechanism of Scheme I requires that

$$F_S = 100 - F_T \quad (6)$$

one can inspect the results for internal consistency by a comparison of the result from eq 5 with that from eq 4 and 6.

Table II shows the "marker" products from each of the olefins. Clearly, the best "markers" will be those adducts the yield of which is most sensitive to changes in the reaction conditions. For three of the olefins, more than one "marker" is available. Only in the case of methyl acrylate, where our GC analysis does not permit simultaneous monitoring of adduct

Table IV. Pairwise Relative Reactivities of Olefins (*i* and *j*) toward Diyl 1

run	F_S^a	$100 - F_S$	F_T^b	F_S^a	$100 - F_S$	F_T^b	$n k_i / n k_j$	
							$n = S$	$n = T$
		$i = \text{CH}_2=\text{CHCN}$				$j = t\text{-XCH}=\text{CHX}$		
1	79	21	26	99	1	3	0.047	0.51 ^c
2	61	39 ^d	29	96	4	6	0.044	0.45 ^c
3	31	69	67	89	11	14	0.047	0.65
4	16	84	86	80	20	24	0.034 ^c	0.60
5	4	96	92	55	45	53	0.024 ^c	0.56
		$i = \text{CH}_2=\text{CHCN}$				$j = c\text{-XCH}=\text{CHX}$		
6	18	82	83	61	39 ^d	45, e 31 ^f	4.6	34.5
7	35	65	64	78	22 ^d	26, 14	4.7	29.3
8	28	72	70	80	20 ^d	29, 16	4.2	41.3
		$i = \text{CH}_2=\text{CHX}$				$j = t\text{-XCH}=\text{CHX}$		
9	45 ^g		55	83	17	21	0.033	0.160
10	35 ^g		65	75	25	18	0.030	0.231
11	45 ^g		55	90	10	14	0.027	0.224
		$i = \text{CH}_2=\text{CHX}$				$j = c\text{-XCH}=\text{CHX}$		
12	7 ^g		93	51	49 ^d	51, 48	0.94	13.0
		$i = \text{CH}_2=\text{CHX}$				$j = \text{CH}_2=\text{CHCN}$		
13	58 ^g		42	50	50	62	0.63	0.28

^a Fraction of product from this olefin that has the limiting "singlet" composition. ^b Fraction of product from this olefin that has the limiting "mostly triplet" composition. ^c This figure is less reliable than the others in its column because less than 15% of one olefin reacted with this diyl spin state. ^d The indirect value ($100 - F_S$) rather than F_T was used to calculate the triplet reactivity. ^e Calculated from tF_1 . ^f Calculated from tB . ^g Calculated from $100 - F_T$.

F_3 and the adducts of the competing olefin, is the dissection limited to one "marker".

Using expressions analogous to eq 4–6, F_S and F_T for each olefin in each competition experiment are calculated from the observed "marker" product distributions. The singlet and triplet relative reactivities for olefins *i* and *j* are given by eq 7 and 8. Table IV summarizes the experiments and calculations for five of the six possible pairwise competitions of the four olefins.

$$S k_i / S k_j = (R_i / R_j) (F_{S(i)} / F_{S(j)}) \quad (7)$$

$$T k_i / T k_j = (R_i / R_j) (F_{T(i)} / F_{T(j)}) \quad (8)$$

The remaining competition experiment provides the ratio of singlet reactivities of dimethyl maleate and dimethyl fumarate. The experiments involve oxygen-saturated reaction mixtures containing high concentrations of olefins, conditions that favor exclusive singlet capture.^{2,4} Table V shows the product distributions obtained from pure maleate, pure fumarate, and a 39.6:1 maleate:fumarate mixture. Peaks 1 and 4 can be used as "markers" for respectively fumarate-derived and maleate-derived product. The contribution from fumarate to the observed peak 3 intensity in the competition experiment thus is $(33)(43/54) = 27.7\%$, whereas that from maleate is $(21.4)(43/57) = 16.1\%$. The calculated peak 3 intensity thus is 43.8%, as compared to the observed value of 44% (Table VI).

The ratio of singlet reactivities of fumarate and maleate then is obtained by summation of the fumarate (63%) and maleate (37%) contributions and multiplication of their ratio by the ratio of olefin concentrations: $S k_i / S k_j = 39.6(63/37) = 67$.

This completes the six possible pairwise comparisons of the four olefins. Table VII summarizes the average dissected reactivities, by pairs, of these olefins.

Note that in the competitions acrylonitrile vs. dimethyl fumarate the fumarate adduct composition shows that the latter olefin reacts almost exclusively with the singlet diyl, even though the reaction competitor is relatively sluggish. Thus it is expected that any olefin whose gross reactivity is greater than that of dimethyl fumarate also should give exclusively singlet reaction products at high concentrations. It is therefore justifiable to assume that the *gross* reactivities of olefins more reactive than dimethyl fumarate are, in fact, singlet reactivities,

Table V. Limiting Singlet Product Distributions (%) for Dimethyl Fumarate and Dimethyl Maleate, and the Distribution Observed in Competition^a

olefin	peak no. ^b			
	1	2	3	4
fumarate (<i>i</i>)	54	3	43	0
maleate (<i>j</i>)	0	0	43	57
<i>i</i> + <i>j</i> ^c	33	2 ^d	44	21

^a Oxygen saturated. ^b See ref 2 for identification. ^c Mixture of 39.6 parts *j* and 1 part *i*. ^d Calculated in Table VI; not directly integrated.

Table VI. Calculated Contributions in the Fumarate–Maleate Competition

olefin	peak no.			
	1	2	3	4
contribn from fumarate (<i>i</i>)	33	2	28	0
contribn from maleate (<i>j</i>)	0	0	16	21
calcd total	33	2	44	21
obsd	33	2 ^a	44	21

^a Calculated; not directly integrated.

and Table VII lists further competition ratios for three further olefins, maleic anhydride, fumaronitrile, and maleonitrile, that meet this requirement.

The present techniques do not provide the ratio of triplet reactivities for fumarate vs. maleate by direct competition, but an indirect and very approximate value can be derived by taking the quotient of the triplet reactivities of lines 3 and 2 or of lines 6 and 4 of Table VII. The values agree to within about 10%, but the true uncertainty probably is much larger. Some estimate of this uncertainty can be made by examination of the directly observed values of the other ratios in Table VII with those derived by "quotient of ratios" calculations similar to those of the line 1 triplet column. The calculated values differ by an average of about 80% from the observed ones, undoubtedly because of the accumulation of experimental errors implicit in the calculations.

Table VIII shows the reactivities based upon the definition of the reactivity of dimethyl maleate in either spin manifold

Table VII. Pairwise Outcome of Competition Experiments, Dissected into Singlet and Triplet Reactivities toward Diyl 1

line	olefin pair (X = CO ₂ Me)		S_{k_i}/S_{k_j}	T_{k_i}/T_{k_j}
	<i>i</i>	<i>j</i>		
1	<i>t</i> -XCH=CHX	<i>c</i> -XCH=CHX	67	(58, ^a 64 ^b)
2	CH ₂ =CHCN	<i>t</i> -XCH=CHX	0.046	0.60
3	CH ₂ =CHCN	<i>c</i> -XCH=CHX	4.5	35
4	CH ₂ =CHX	<i>t</i> -XCH=CHX	0.030	0.21
5	CH ₂ =CHX	CH ₂ =CHCN	0.63	0.28
6	CH ₂ =CHX	<i>c</i> -XCH=CHX	0.94	13
7	<i>t</i> -XCH=CHX	<i>t</i> -NCCH=CHCN	0.38 ^c	
8	<i>t</i> -XCH=CHX	<i>c</i> -NCCH=CHCN	0.42 ^c	
9	maleic anhydride	<i>t</i> -NCCH=CHCN	1.3 ^c	

^a Obtained indirectly as the quotient of the triplet ratio of lines 3 and 2. ^b Obtained indirectly as the quotient of the triplet ratio of lines 6 and 4. ^c Measured gross relative reactivity.

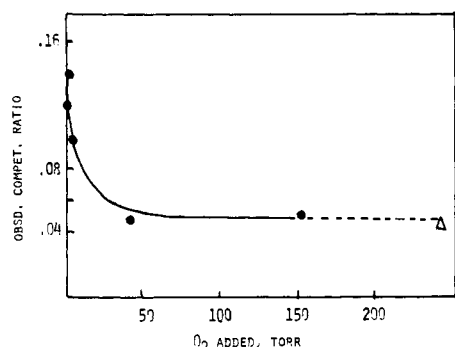


Figure 4. Effect of oxygen on the observed competition ratio acrylonitrile/dimethyl fumarate, initial olefin concentration 0.64 M: ●, experimental points; Δ, dissected singlet competition ratio from Table IV.

as unity. Comparisons of reactivities in the singlet manifold to those in the triplet manifold cannot be made from these data. The Experimental Section describes the basis for the statement that any given competition-derived value in Table VIII is reliable to within about 30%. The four singlet reactivity values (Table III) deduced from the dilution experiments described earlier are included for comparison. The agreement between the two independent methods, comparing parameters that are far removed from the quantities actually observed in the experiments, is surprisingly good.

Effect of Oxygen. The previous work^{2,4a} showed that molecular (triplet) oxygen has a dramatic effect upon the product distributions in the reactions of diyl 1 with olefins, apparently because it preferentially captures the triplet biradical. In competition experiments such as those described here, the gross relative reactivity ratios represent a blend of singlet and triplet ratios. Unless these ratios are fortuitously identical in the pair of competing olefins, oxygen also should change the observed reactivity ratios by scavenging the triplet. At sufficiently high oxygen concentration, the observed competition ratio should approach the singlet value.

Figure 4 shows the oxygen effect on a competition between acrylonitrile and dimethyl fumarate for the intermediates generated by thermal deazetation of the azo compound 8. The total olefin concentration is 0.64 M. In the degassed system, the gross reactivity ratio acrylonitrile/fumarate is 0.14, but as oxygen is admitted the ratio falls sharply and then levels off at about 0.045. The oxygen-saturated value is in good agreement with the ratios of *singlet* reactivities deduced from the dilution experiments of Table III (0.067) and by direct competition (Table IV, 0.046). Clearly, oxygen at pressures above 200 Torr suffices to quench the triplet reaction, leaving the singlet diyl as the only partner for the competing olefins.

Competition Ratios from Photochemically Generated Intermediates. In other work,¹¹⁻¹⁴ we report on the generation of TMM-type intermediates by photolysis of the diazene 8. So

Table VIII. Dissected Relative Reactivities toward Diyl 1

olefin	$S_{k_{rel}}$	$S_{k_{rel}}^a$	$T_{k_{rel}}$
maleic anhydride	235		
maleonitrile	180		
fumaronitrile	160		
dimethyl fumarate	67	48	59
acrylonitrile ^b	4.5, 3.1	3.2	35
methyl acrylate ^b	0.9, 2.0	1.2	12
dimethyl maleate	(1.0)	(1.0)	(1.0)

^a From dilution experiments (Table III). ^b First value, relative to dimethyl maleate, by competition; second value, relative to dimethyl fumarate, by competition.

Table IX. Comparison of Thermal and Photochemical Relative Reactivities (X = CO₂CH₃)

olefin		k_i/k_j	
<i>i</i>	<i>j</i>	thermal	photochem
<i>t</i> -XCH=CHX	<i>t</i> -NCCH=CHCN	0.38	0.42
<i>t</i> -XCH=CHX	<i>c</i> -NCCH=CHCN	0.43	0.43
CH ₂ =CHCN	<i>t</i> -XCH=CHX	0.070	0.068
maleic anhydride	<i>t</i> -NCCH=CHCN	1.3	1.0
CH ₂ =CHCN	<i>c</i> -XCH=CHX	12	12

far, the bulk of the evidence suggests that the intermediates responsible for the singlet products in the photochemical reactions do not differ from those derived thermally. We now offer additional confirmation of this by a comparison of the competition ratios for the two modes of deazetation. In each competition, a solution of diazene 8 and two olefins is divided in two. Half of the solution is pyrolyzed under the previously described conditions (sealed, degassed, 60 °C), and the other half is cooled to 0–8 °C to prevent pyrolysis and photolyzed at 350 nm until all of the diazene is consumed. Table IX shows no significant differences in the derived gross competition ratios.

Discussion

The experimental evidence on the reactions of the singlet species with olefins strongly suggests that both new cycloadduct bonds are formed simultaneously. The highly stereospecific syn addition^{2,4} and the effect of substituents on the reactivity are both reminiscent of the Diels–Alder reaction. Figure 5 shows the correlation between the Diels–Alder dienophilicities of seven olefins toward cyclopentadiene¹⁸ and their diylphilicities toward the singlet TMM species. Although it would be desirable to have more points at intermediate reactivities, it seems clear that the correlation breaks down at high reactivity, maleic anhydride (A) being a less reactive singlet diylophile than would be predicted from a linear extrapolation of the correlation line. This deviation could conceivably be caused by absolute rates of olefin-singlet re-

Table X. Comparison of Relative Reactivities of Olefins in Four Types of Addition Reactions

olefin ^a	$S_{k_{rel}}$	Diels-Alder ^b	$T_{k_{rel}}$	copolym ^c
maleic anhydride	235	8850		208
<i>t</i> -NCCH=CHCN	180	150		44
<i>t</i> -XCH=CHX	67	118	58	39
CH ₂ =CHX	1	1.9	35	11
CH ₂ =CHCN	4	1.7	12	21
<i>c</i> -XCH=CHX	(1)	(1)	(1)	(1)

^a X = CO₂Me. ^b Relative rate of Diels-Alder reaction with cyclopentadiene (ref 18). ^c Relative rate of reaction with a growing polystyrene radical in copolymerization (ref 22).

Table XI. GC Columns Used

A	10 ft × 1/8 in. 2% XE-60 on 100/120 mesh silanized Chromosorb P
B	10 ft × 1/8 in. 1% XE-60 on 100/120 mesh silanized Chromosorb P
C	10 ft × 1/8 in. 2% EGP on silanized 100/120 Chromosorb P
D	5 ft × 3/8 in. 20% Carbowax 20M on 60/80 Chromosorb P
E	5 ft × 1/4 in. 5% XE-60 on 60/80 Chromosorb P
F	234 ft × 0.01 in. tris(cyanoethoxy)propane capillary
G	200 ft × 0.01 in. Carbowax 20M capillary
H	6 ft × 1/4 in. 40/60 molecular sieves (Linde 13X)
I	20 ft × 3/8 in. 20% FFAP on 60/80 Chromosorb P
J	20 ft × 1/4 in. 20% OV-225 on 70/80 mesh Anakrom ABS

action at the upper end of the reactivity scale that approach the encounter-controlled limit.³ Were this the case, the diylphilic reactivities would tend to a plateau; all of the diylphiles studies here have roughly the same diffusion coefficient, and the rates would therefore become insensitive to structure. Another possible reason for the leveling off at high diylphilicity might be the existence of a reversible reaction between the open (**1-S**) and closed (**10**) forms of the singlet. This could



cause a switch in the rate-determining step for cycloadduct formation, from the capture of **1-S** when the diylophile is weak to the formation of **10** when the diylophile is strong. In the latter limit, all sufficiently strong diylphiles would appear equally reactive. Further study is needed to elucidate the observed leveling effect.

Although the concept of a concerted cycloaddition to olefins is compatible with a formulation of the reactive singlet as the diyl **1-S**, nothing in the present work excludes the possibility that the true reactive singlet may be the bicyclic hydrocarbon, **10**. The chemistry of the latter species is just beginning to be explored,¹⁴ and we defer further discussion of the experimental distinction between **1-S** and **10** as the cycloaddition intermediate.

Nevertheless, regardless of which form is the actual reactant, the very high regioselectivity of the cycloaddition for fused product supports the concerted mechanism.^{3,19-21}

In contrast, the cycloadditions of the triplet appear to be nonconcerted. These reactions are neither regioselective nor stereospecific. If the reaction occurs in two steps, initial attack by the olefin at a diyl ring position would be twice as probable on statistical grounds as attack at the exocyclic position. The intermediate **11** formed by attack on the ring has a probability of 50% for closure at the other ring position to give bridged product and 50% for closure at the exocyclic position to give fused product, whereas the intermediate **12** formed by initial attack at the exocyclic position must close to fused product.

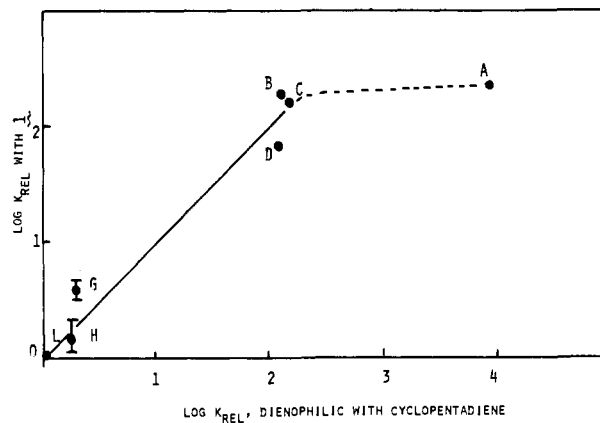
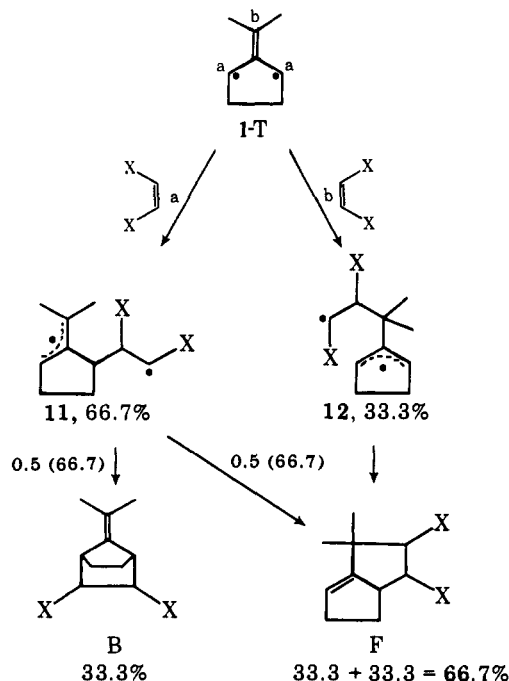


Figure 5. Relationship of dienophilic reactivity of olefins reacting with cyclopentadiene against their diylphilic reactivity in reaction with the singlet TMM biradical **1**. The letters identify the olefins maleic anhydride (A), maleonitrile (B), fumaronitrile (C), dimethyl fumarate (D), acrylonitrile (G), methyl acrylate (H), and dimethyl maleate (L).

Thus, F/B would be 2 if the reaction were merely statistically controlled. The observed values for dimethyl fumarate and dimethyl maleate (0.72), acrylonitrile (3.0), and methyl acrylate (2.5) show at most a feeble deviation from statistical behavior. Moreover, the stereochemistry of the triplet cycloadduct mixture from fumarate and maleate is nearly randomized, the fumarate and maleate products being 92:8 and 88:12 trans:cis, respectively.



The reactivity order of olefins toward the triplet also suggests a nonconcerted cycloaddition. The first step is the addition of a radical center to an olefin, and one might expect some correlation with the rates of such additions of simple radicals. Table X collects the relative singlet and triplet diylphilicities of the olefins used in this study and compares them with the Diels-Alder data just discussed as well as a set of relative rate constants of monoradical-olefin additions. The free-radical addition data are the relative reactivities of the olefins toward the growing polystyrene radical in copolymerization.^{22,23} Although the order of the radical additions is qualitatively similar to the singlet diylphilic and Diels-Alder dienophilic orders, closer inspection indicates that the two monosubstituted olefins, methyl acrylate and acrylonitrile, are relatively about

Table XII. Retention Time of Olefin Adducts of **1** and of Internal Standards

column	temp	olefin	adduct ret time, min	int std
B	140 °C 37 min 4 °C/min to 190 °C	dimethyl fumarate	30.3	18.8 ^a
			44.4	
	fumaronitrile	49.1		
		51.1		
	maleonitrile	49.0		
C	175 °C		51.1	
			73.5	
			75.3	
		fumaronitrile	24.4	
		maleic anhydride	26.0	52.7 ^b
A	125 °C, 41 min 4 °C/min to 150 °C		29.5	
			31.1	
			37.4	
		acrylonitrile	28.5	52.7 ^a
			29.9	
B	105 °C		33.1	
			38.9	
		dimethyl fumarate	68.9	
			74.7	
		methyl acrylate	17.8	
			19.3	
			20.1	
			23.8	
		acrylonitrile	30.2	
			31.9	
B	110 °C		35.8	
			43.5	
		methyl methacrylate	18.2	
			22.3	
			23.7	
			25.5	
		methacrylonitrile	22.4	
	31.5			
			34.0	

^a 2-Methoxynaphthalene. ^b Di-*tert*-butyl phthalate. Conditions: Perkin-Elmer 900 analytical VPC; oven temperature as shown; injector 180 °C, manifold 200 °C, 35 psig N₂ flow except column A, 50 psig.

tenfold more reactive toward the polystyrene radical (Table X). Dimethyl fumarate enjoys substantial advantages over both methyl acrylate and acrylonitrile in the concerted cycloadditions (singlet and Diels-Alder), the ratios of rates being respectively 67 and 62 times those for methyl acrylate and 17 and 70 times those for acrylonitrile. In the radical additions (triplet cycloaddition and polystyrene radical copolymerization), the ratios fall to 1.7 and 4.8 relative to methyl acrylate and 3.5 and 1.9 relative to acrylonitrile. The close parallel in the compression of the reactivity scale lends credence to the assignment of a stepwise mechanism to the cycloaddition of our triplet diyl to olefins.

Experimental Section

Procedures for pyrolyses of olefin-diazene solutions have been described elsewhere.² The photochemical reactions were carried out by immersion of the sample tubes in a spoutless beaker of ice-water which was in turn placed into an unsilvered Dewar cylinder containing more ice-water and irradiated in a Rayonet photochemical reactor for 1 h with 16 350-nm lamps. The temperature of the bath water never exceeded 8 °C. Control experiments showed that this period of irradiation sufficed to photolyze >99% of the diazene.

Analysis of the products was achieved as before.² The GC columns used are listed in Table XI.

Retention Times of Adducts. Since the columns were used at different temperatures for different analyses, both because of their deterioration mentioned above and also because different pairs of olefins required different conditions, no absolute set of retention times is available. However, the number and relative proportions of the isomers

Table XIII. NMR Data for Hydrogenated Diels-Alder Adducts (**11**) of 6,6-Dimethylfulvene and Olefins

11

olefin	m	p	q	other
methyl acrylate	1.68		1.2-2.06	<i>a</i>
methacrylonitrile	1.70, 1.74	2.70	1.0-2.0	1.37 (s, 3, methyl)
maleic anhydride (endo adduct)	1.70	3.20 (t, <i>J</i> = 2)	1.58 (d, <i>J</i> = 2.8)	2.98 (s, 2, α to C=O)
dimethyl maleate (exo adduct)	1.68	2.94 (t, <i>J</i> = 2)	1.1-1.6	2.75 (s, 2, α to C=O) 3.56 (s, 6, CO ₂ CH ₃)
maleonitrile	1.92, 1.77	3.17, 3.25	1.2-2.2	2.97 (s, 2, α to CN)
acrylonitrile	1.85, 1.76, 1.81	2.92, 3.17	1.2-2.2	2.60 (t?, <i>J</i> = 3.8, α to CN)
methyl methacrylate	1.60, 1.68	2.60	1.0-1.8	1.15, 1.25 (m, 3, methyl) 3.62, 3.68 (s, 3, CO ₂ CH ₃)

^a 2.38, q, 1 (*J* = 2), 2.68, 2.90 (3). *J* values in hertz.

of any olefin's adducts were so distinctive that, once identified, no difficulty was found in identifying the products under a variety of conditions.

Because of the greatly differing molecular weights and polarities of the adducts from different olefins, temperature programming was usually required during an analysis. In Table XII, showing the representative retention times of the center of the cluster of adducts from an olefin, a temperature program is indicated thus: 110 °C - 23 min, 4 °C/min to 160 °C indicates an analysis where the temperature is held at 110 °C for 23 min, after which it is increased by 4 °C/min to 160 °C, where it is held for the rest of the analysis.

Identification of products in the competition runs rested on GC retention time (coinjection of a synthetic bridged isomer giving a peak enhancement) and mass spectrometry of the effluent stream using a Perkin-Elmer 990 GC coupled to a Hitachi Perkin-Elmer RMU single-focusing mass spectrometer. In each case, all well-resolved peaks showed a parent ion at *m/e* corresponding to the sum of the molecular weights of the olefin and biradical (mol wt for dimethyl diyl **1** is 108), indicating the formation of a 1:1 adduct. Fragmentation patterns were not quantitatively analyzed since the rapid scanning rates and changing concentrations in the ionization chamber of the mass spectrometer, inherent in VPC-MS, prevent reliable data on intensities.

Diels-Alder Adducts of 6,6-Dimethylfulvene and Olefins. The following standard procedure was used. In 15 mL of benzene were placed 10 mmol of the appropriate olefin with 2.0 g of 6,6-dimethylfulvene, and the solution was heated at reflux overnight. The benzene was then removed by rotary evaporation. Purification was postponed until after hydrogenation. The adducts of 6,6-dimethylfulvene with maleic anhydride and acrylonitrile are known¹⁵ compounds.

Hydrogenation of the Diels-Alder Adducts of 6,6-Dimethylfulvene and Olefins. The following standard procedure was used. The entire product of the Diels-Alder reaction was dissolved in 50 mL of ethyl acetate, and 200 mg of 10% palladium on charcoal was added. The solutions were then hydrogenated at atmospheric pressure, taking up 1 equiv (ca. 450 mL) of hydrogen in (typically) 1 h. Table XIII summarizes the NMR data for the products.

Table XIV. NMR Spectral Data for Adducts of Diyl 1 and Acrylonitrile

isomer	methyl	-CH ₂ -	allylic	α to CN	bridgehead	vinyl
F ₁	1.269 (s, 3)	1.394 (q, 1)	1.9-2.7 (m, 11) ^a	3.369 (br, 1)	5.368 (s, 1)	
	1.201 (s, 3)	1.516 (dt, 1)		3.208 (br, 1)	5.305 (s, 1)	
	1.173 (s, 3)	1.732 (m, 1)				
	1.133 (s, 3)					
F ₂	1.296 (s, 3)	1.443 (q, 2)	2.532 (br, 2)	2.843 (t, 1)	2.995 (br, 1)	5.359 (s, 1)
	1.201 (s, 3)	2.138 (br, 1)				
		2.279 (br, 1)				
F ₃	1.261 (s, 3)	1.906 (dq, 1)	2.606 (br d, 2)	3.009 (dt, 1)	3.328 (br, 1)	5.380 (s, 1)
	1.086 (s, 3)	2.115 (m, 3)				
B	1.647 (s)					

^a Chemical shifts were measured in deuteriochloroform and are given in parts per million downfield from tetramethylsilane. Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad.

Table XV. NMR Spectral Data for Adducts of Diyl 1 and Methyl Acrylate

isomer	Me	-CH ₂ -	allylic	α to CO ₂ Me	bridgehead	vinyl	CO ₂ Me
F ₁	1.1 (s, 6)	1.3-1.6 (m, 4)	2.1 (m, 2)	2.45 (m, 1)	3.2 (br, 1)	5.2 (s, 1)	3.6 (s, 3)
F ₂	0.991 (s, 3)	1.318-1.641 (m, 2)	2.266-2.649 (m, 2)	2.837 (q, 1)	2.863 (br, 1)	5.231 (s, 1)	3.663 (s, 3)
	1.263 (s, 3)	1.910-2.110 (m, 2)					
F ₃	1.047 (s, 3)	1.319-2.132 (m, 4)	2.303-2.532 (m, 2)	3.0-3.2 (m, 1)	3.415 (br, 1)	5.264 (dd, 1)	3.643 (s, 3)
	1.210 (s, 3)						
B ₂	1.642 (s, 3)	0.9-1.6 (m, 6)		2.756 (p, 1)	2.903 (t, 1)		3.687 (s, 3)
	1.666 (s, 3)				2.625 (t, 1)		
B ₁	1.63 (s)						3.620 (s)
	1.64 (s)						

Isolation of Fused Adducts from Diyl-Olefin Reactions. The fused adducts from maleic anhydride, dimethyl maleate, and dimethyl fumarate already have been described.² In the cases of acrylonitrile¹⁶ and methyl acrylate¹⁶ the fused products were isolated as follows.

Preparative-Scale Reaction of Diazene 8 and Acrylonitrile. A mixture of 0.4 g of diazene 8 and 7 g of acrylonitrile was placed in a 10-mL volumetric flask and diluted to the mark with acetonitrile. The solution was placed in a pyrolysis flask, degassed and sealed as in the small-scale reaction, and pyrolyzed for 8 h at 60 °C. The adducts were separated by preparative VPC on column J at 135 °C and 30 psi. NMR spectra were taken in micro NMR tubes on the Bruker 270-MHz instrument and are reported in Table XIV.

Preparative-Scale Pyrolysis of Diazene 8 and Methyl Acrylate. A mixture of 0.509 g of diazene 8 and 6.449 g of methyl acrylate was placed in a 10-mL volumetric flask and diluted to the mark with acetonitrile. The solution was placed in a pyrolysis tube, degassed and sealed, and pyrolyzed at 60 °C for 8 h. The adducts were separated into three fractions on column J at 160 °C and 30 psi. The middle fraction, a mixture of F₂, F₃, and B₁, was then again separated into three fractions on column J at 135 °C and 30 psi. However, the adducts were not well separated. NMR spectra were taken in micro NMR tubes on the Bruker 270 instrument and are reported in Table XV.

In the case of fumaronitrile,¹⁷ a mixture of 0.55 g of the nitrile, 1.56 g of diazene 8, and 8 mL of dry acetonitrile was stirred at 46-48 °C for 3 days and then at 25 °C for 12 h. After removal of the solvent on the rotary evaporator, the residue was chromatographed on Florisil with petroleum ether and ethyl ether to remove colored impurities. After the solvent was again removed, the residue was distilled at ~0.2 mmHg for 28 h with a dry ice trap to collect fumaronitrile. The yellow, oily residue was triturated with MeCN to remove a small amount of contaminating silicone grease. Removal of the MeCN by evaporation left 0.759 g of crude product. GC (5 ft × 1.8 in., 1% XE60) showed 4% short retention time impurities, 94.6% adducts, and 1.4% of a long retention time impurity. The calculated yield was 95% of two fumaronitrile adducts. The adducts were purified by preparative VPC (10 ft × 1/4 in. 10% XE60 on Chromosorb W AW-DMCS, 185 °C) to give pure isomers A, a white solid, and B, an oil that could be induced to solidify when scratched, in order of retention time, each >98% pure.

Adduct A, mp 82-86 °C. NMR (100 MHz): δ 5.50, q, $J \sim 2$ Hz, 1 H vinyl; 3.46, m, 1 H, allylic methine; 3.33, dd, $J \sim 8, 10$ Hz, 1 H, α to CN; 2.86, d, $J = 8$ Hz, 1 H, α to CN; 2.54, m, 2 H, CH₂; 2.23, m (at least 10 lines), 1 H, methylene H; 1.85, m, 1 H, methylene H;

1.34, s, 3 H, CH₃; 1.19, s, 3 H, CH₃. The coupling constants of the δ 3.33 resonance were evaluated on a sample treated with Eu(fod)₃.

Anal. Calcd for C₁₂H₁₄N₂: C, 77.38; H, 7.58; N, 15.04. Found: C, 77.33; H, 7.54; N, 15.04.

Adduct B: δ 5.44, q, $J \sim 2$ Hz, 1 H, vinyl; 3.34, m, 1 H, allylic methine; 3.16, d, $J = 10.2$ Hz, 1 H, α to CN; 2.60, m, 2 H, methylene H; 2.53, t, $J = 10.5$ Hz, 1 H, α to CN; 2.30, m, 1 H, methylene H; 1.62, m, 1 H, methylene H; 1.30, s, 6 H, CH₃. The coupling constant of the δ 2.53 peak was evaluated on a sample treated with Eu(fod)₃.

Anal. Calcd for C₁₂H₁₄N₂: C, 77.38; H, 7.58; N, 15.04. Found: C, 77.32; H, 7.56; N, 15.08.

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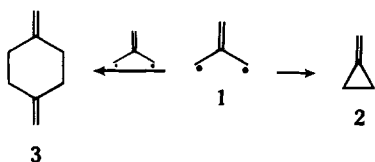
Direct Measurements of the Absolute Rates of Dimerization and Capture of the 2-Isopropylidenecyclopenta-1,3-diyl Species by Electron Paramagnetic Resonance Spectroscopy

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Abstract: The disappearance of the triplet electron paramagnetic resonance (EPR) signal of 2-isopropylidenecyclopenta-1,3-diyl in a propanolic medium at 143.6 K is a second-order reaction. Its rate can be measured with an accuracy of about 50% by EPR spectroscopy and is found to be approximately 0.13 times the diffusion-controlled encounter frequency. This is too fast to permit the mechanism to be a combination of the diyl singlet with the triplet and is consistent with a triplet-triplet dimerization. The rates of cycloaddition of the triplet diyl to olefins also can be measured by EPR techniques are best interpreted as the result of a stepwise triplet plus olefin reaction, in which the two new bonds of the cycloadduct are formed sequentially rather than simultaneously.

Although the parent trimethylenemethane (TMM) biradical **1** apparently can be generated by several different reactions,² under most conditions, the species cyclizes to methylenecyclopropane (**2**) rather than dimerizes to 1,4-bis(meth-



ylene)cyclohexane (**3**). The exceptions to this behavior are of special interest as possible indicators of the electronic spin state of the reactant **1**. Thus, the observations that the dimeric product **3** is present in the reaction mixtures from 2-iodomethylallyl iodide and potassium vapor³ and from the benzene-sensitized photolysis of 4-methylenepyrazoline⁴ have been interpreted as manifestations of the involvement of triplet **1**.

The substituted TMM, 2-isopropylidenecyclopenta-1,3-diyl (**4**), generated from the diazene **5**, offers an especially attractive vehicle for the study of TMM dimerizations because, in contrast to the parent TMM (**1**),⁵ the triplet ground state^{6,7} of diyl **4** does not cyclize intramolecularly but gives high yields of dimers **6-9**. The singlet diyl **4-S** cyclizes to the bicyclic hydrocarbon **4-C**,^{6c} but **4-C** is thermally stable at the temperatures (120-144 K) encountered in the present work and hence cannot be a source of **4-Tr**.

The present paper describes direct measurements of the absolute rates of dimerization and cycloaddition of diyl **4** by electron paramagnetic resonance (EPR) spectroscopy. The results favor a triplet + triplet (rather than singlet + triplet or singlet + singlet) reaction as the major mechanism of dimer formation. Supplementing previous competition measurements^{8,9} of the relative reactivities toward triplet **4** of olefinic trapping agents to give adducts, the present work also gives relative reactivities from the ratios of absolute reactivities and offers independent support for the earlier conclusions.

