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## References and Notes

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- See footnote a, Table I, p 1-273.

## Dimerization and Cycloaddition Reactions of a Trimethylenemethane Derivative, 2-Isopropylidenecyclopenta-1,3-diyl. Mechanistic Separation of Triplet and Singlet Reactions

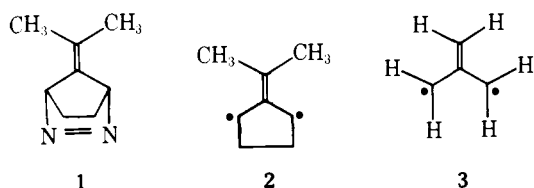
Leonard R. Corwin, Dale M. McDaniel, Richard J. Bushby, and Jerome A. Berson\*

Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06520. Received June 11, 1979

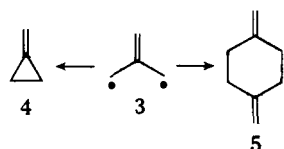
**Abstract:** Pyrolysis of 7-isopropylidene-2,3-diazanorbornene (**1**) at 60 °C in solution liberates N<sub>2</sub> and 2-isopropylidenecyclopenta-1,3-diyl (**2**). The diyl (**2**) dimerizes readily, but, in the presence of an olefinic trapping agent, **2** can be intercepted as either a fused adduct, **F**, a bicyclo[3.3.0]oct-1-ene, or a bridged adduct, **B**, a 7-isopropylidenenorbornane. The composition of the adduct mixture is dependent on the initial concentration of the trapping olefin, fused adducts being heavily favored at high concentrations. The concentration dependence arises from two forms of the diyl which are generated sequentially in a cascade mechanism. The first species is a singlet that can add both regiospecifically and stereospecifically, whereas the second is the triplet ground state of the diyl. Quantitative treatment of the dilution effect data for the addition of dimethyl fumarate leads to the conclusion that the rate constants for capture of the singlet and intersystem crossing to the triplet are in the ratio 7.7 M<sup>-1</sup>.

The diazene **1**, 7-isopropylidene-2,3-diazanorbornene, is a source of 2-isopropylidenecyclopenta-1,3-diyl, **2**, a trimethylenemethane (TMM) derivative.<sup>2</sup> Diyl **2** incorporates part of the  $\pi$ -electron conjugated system of the parent TMM **3** in a five-membered ring, a structural feature that we believed might have useful application in fostering cycloaddition reactions.

Generation of reactive intermediates presumed to be the parent TMM, **3**, has been achieved by several routes. The two major reactions of **3** seem to be cyclization to methylenecyclopropane, **4**,<sup>3-13</sup> and [3 + 3] dimerization to 1,4-bismethylenecyclohexane, **5**.<sup>6,10-12,14,15</sup> The dimerization to **5** apparently is a characteristic reaction of the triplet form of **3**,<sup>9,16</sup> whereas ring closure to **4** can occur from triplet **3**<sup>12b</sup> and pre-



sumably also from singlet **3**. Although putative TMM species occasionally undergo cycloaddition reactions with olefins in low to moderate yields,<sup>6,12a,15,17</sup> intramolecular ring closure frequently dominates the chemistry of **3** and has made it difficult to trap the diyl effectively.

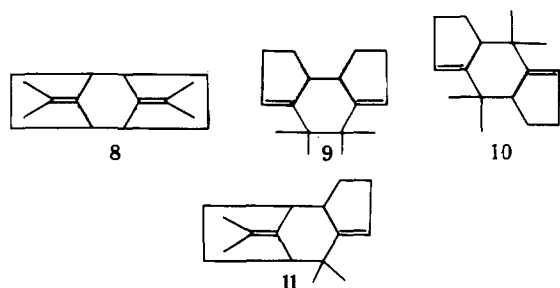


The perceived advantage of the cyclic TMM **2** lies in the hope that intramolecular cyclization to either of the highly strained methylenecyclopropanes, **6** or **7**, would be disfavored,



either kinetically or thermodynamically. This should make the bimolecular capture of TMM **2** easier than that of the parent diyl, **3**. Whatever the underlying cause, this line of reasoning has proven fruitful, because, as we report here and elsewhere,<sup>18</sup> intermolecular capture of **2** and other 2-alkylidenecyclopentadiyls by olefins in fact is an extremely efficient reaction.

**Thermal and Photochemical Decomposition of Diazene 1. Formation of Dimers of TMM 2.** The diazene **1** is a low-melting, white crystalline material. It turns brown upon storage in the solid state but can be kept in ether or chloroform at  $-20^{\circ}\text{C}$  for weeks with only minor losses. Its solutions smoothly evolve nitrogen above  $40^{\circ}\text{C}$  to give high yields of dimeric products resulting from the four different ways (**8–11**) of



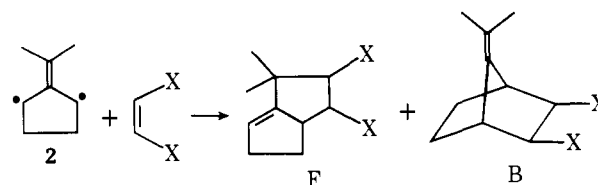
combining two TMM units of structure **2**. The assignments of structure to **8–11** are based upon mass spectra and proton NMR spectra. In particular, each dimer shows a weak parent mass peak at  $m/e$  216 and very strong peaks at  $m/e$  107, 108, and 109. Two of the dimers (**9** and **10**) show two olefinic resonances near  $\delta$  5.3, one (**11**) shows one, and one (**8**) shows none. The methyl resonances for **9** and **10** all occur near  $\delta$  0.8–0.9, whereas those for **8**, being allylic, occur at lower field,  $\delta$  1.75. Compound **11** has a pair of each kind and shows two low-field ( $\delta$  1.73) and two high-field ( $\delta$  1.11) methyl resonances. The dimers are formed in the approximate proportions 22% of **8**, 35% of **9** and **10**, and 44% of **11**.

In principle, each of the dimers can exist in two stereoisomeric forms, so that a total of eight isomers might be expected. Under certain analytical gas chromatographic (GC) conditions, it is possible to detect as many as six peaks in the dimer mixture, and it is not out of the question that all eight isomers are formed.

Because our GC analyses apparently do not resolve all the dimers, we cannot be sure that the product composition is strictly invariant under all conditions of generation of the diyl **2**, but, within the experimental limitations, no gross changes can be observed, regardless of whether the diazene **1** is decomposed thermally (gas phase or solution) or photochemically (solution). Moreover, we do not detect any change when a substantial portion of the diyl is captured by olefins. The portion that escapes such capture still dimerizes in the same ratio as before.

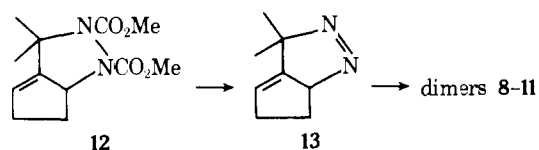
When a *m*-dichlorobenzene solution of the diazene **1** is placed into the preheated probe of an NMR spectrometer ( $102\text{--}145^{\circ}\text{C}$ ), the proton resonances for the product dimers all appear within a few seconds as strongly inverted signals. This chemically induced dynamic nuclear polarization (CIDNP) emission persists for a few dozen seconds, the strength and duration of the effect being dependent on the reaction temperature. After a few minutes, the emissions decay and are replaced by the much weaker normal absorptions of the product dimers. Closs<sup>19</sup> has extended the radical-pair theory of CIDNP to this case and has concluded that polarization can occur only if at least one of the reacting diyl partners is a triplet. The theory and experiments may be said to provide the first direct physical evidence for the involvement of a triplet TMM in a chemical reaction. Later studies by ESR kinetic measurements<sup>20</sup> have shown that the dimerization is largely a triplet-triplet reaction.

**Capture of Diyl 2 by Olefins.** The dimerization of diyl **2** can be completely suppressed by carrying out the thermal deazetation of diazene **1** in a solution containing a sufficiently high concentration of an olefinic trapping agent. Although low yields of cycloadducts of diyl **2** and some simple olefins can be obtained, for example, with *cis*- or *trans*-1,2-dichloroethylene, conjugated olefins are much more efficient traps. High yields of adducts with the general structures F and B (fused and bridged) result from reactions with 1,3-dienes, aromatic olefins (styrene, stilbene), and  $\alpha,\beta$ -unsaturated esters, nitriles, or anhydrides.



Conjugated acetylenes do not seem to be useful for this purpose, giving a small yield of diyl dimers and a large quantity of dark, polymeric material. One reason for the failure to achieve cycloaddition with acetylenes may be a side reaction between the diazene and the acetylene, *before* deazetation, although we have not established this point.

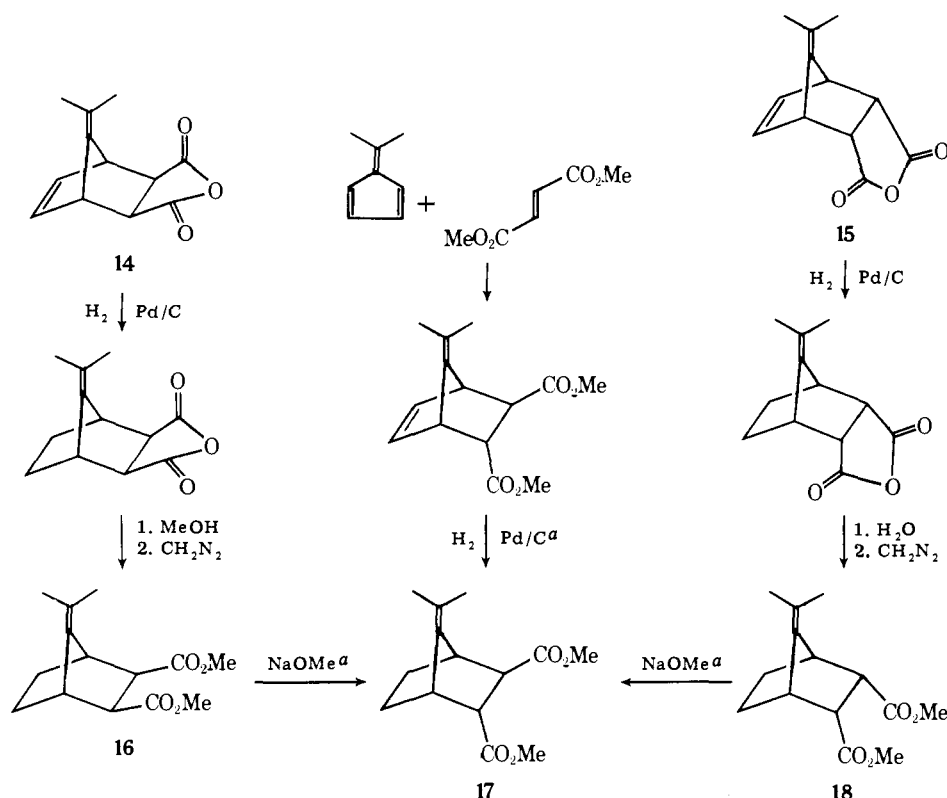
Dimethyl azodicarboxylate also is a fairly efficient trapping agent. It gives largely the fused adduct **12**, isomeric with the bridged carbamate that is the precursor of diazene **1**. The fused carbamate **12** can be converted by the usual<sup>2</sup> hydrolysis-de-



carboxylation-oxidation sequence to a new diazene **13**, isomeric with **1**. Thermal deazetation of **13** yields the same set of diyl dimers **8–11** in the same proportions as obtained from **1**.

The next section describes the structural assignments to the cycloadducts of diyl **2** and olefins. Readers to whom these

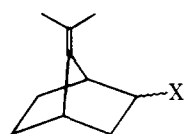
Scheme I



<sup>a</sup>This work. Other reactions from ref 21.

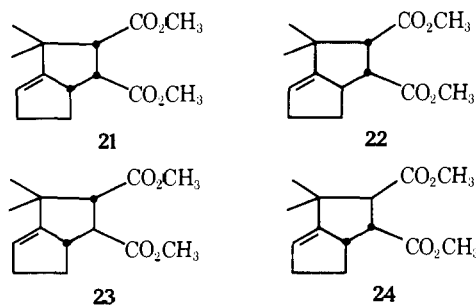
details of secondary interest may pick up the thread of the mechanistic analysis by skipping to the section on the dilution effect.

**Structures of the Adducts in the Maleate-Fumarate Series.** The adducts in the bridged diester series, B, X = CO<sub>2</sub>CH<sub>3</sub> (**16**, **17**, and **18**), are identified by independent synthesis from the known<sup>23</sup> Diels-Alder adducts of dimethylfulvene and maleic anhydride, **14** and **15**, by the straightforward chemical correlations shown in Scheme I. Similar correlations lead to assignments of the bridged structures in the bridged monomer (**19**) and nitrile (**20**) series.



**19**, X = CO<sub>2</sub>Me  
**20**, X = CN

In the fused series, the assignments rest upon NMR spectroscopy. In principle, four isomers, **21-24**, are possible, and

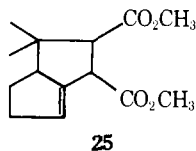


all four are observed in the reaction of diyl **2** with dimethyl maleate. Two of the isomers, cF<sub>1</sub> and cF<sub>2</sub>, numbered in order of their GC elution, have the cis configuration of the X groups, and two, tF<sub>1</sub> and tF<sub>2</sub>, have the trans. A complete assignment

of stereochemistry is not yet available, but it is clear which adducts correspond to the cis structures (**21** and **22**) and which to the trans (**23** and **24**). We can base a preliminary hypothesis on the assumption that the cycloadditions, if at all stereospecific, should occur by predominant syn addition to the double bond, so that, under the proper conditions, dimethyl maleate should lead to a predominance of the cis-fused isomers **21** and **22**, whereas dimethyl fumarate should give mainly the trans-fused products, **23** and **24**. In fact, the reactions are stereospecific at high concentrations of the trapping olefin, and different pairs of fused adducts predominate from maleate and fumarate. In an extension of this reasoning, it would be expected that maleic anhydride should favor syn addition, since in contrast to the diester reactions, even a step-wise mechanism would pass over an intermediate that could not lose stereochemistry by internal rotation about the former olefinic bond. Stepwise antiaddition, although not precluded, would require relative motion of large moieties, would lead to more strained products, and therefore should be less favorable. The two fused adducts isolated from the maleic anhydride reaction in fact have the same stereochemistry as the two cis diester adducts, **21** and **22**, since the anhydrides can be converted to the diesters by successive treatment with neutral methanol and diazomethane. Moreover, epimerization of the cis diesters with methanolic sodium methoxide rapidly gives mixtures containing the trans adducts. The trans adducts slowly interconvert with each other under the same conditions (more rapidly at higher temperature) but do not form significant amounts of cis. Although equilibrium may not have been reached from both directions, the relative epimerization rates suggest that the diesters assigned the trans structures are the more stable ones, as would be expected on steric grounds.

Although they do not provide a firm basis for stereochemically matching the members of the pairs of compounds, e.g., cF<sub>1</sub>-cF<sub>2</sub> with the pairs of structures, e.g., **21-22**, the NMR spectra of the fused adducts **21-24** all show a vinyl proton resonance near  $\delta$  5.3, which immediately distinguishes these

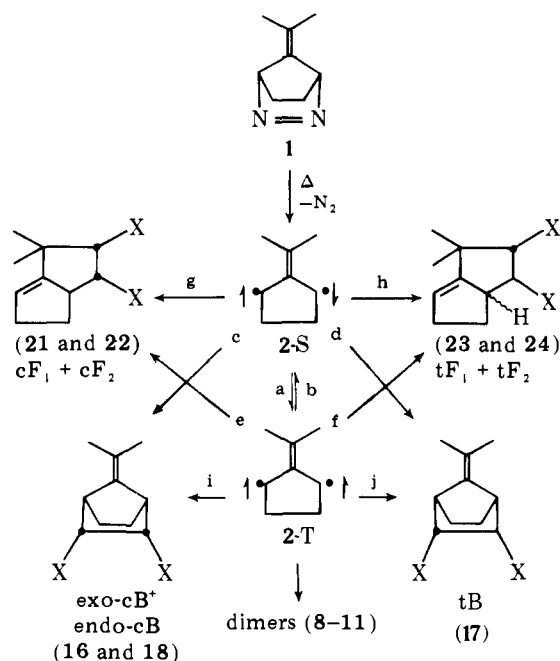
substances from the bridged adducts **16–18**. Other features of the spectra are consistent with the assigned structures. In particular, the presence in the fused adducts of two non-equivalent *gem* methyl groups is manifested by pairs of resonances near  $\delta$  1.0 and 1.3 (except for  $\text{cF}_2$ , in the spectrum of which the absorptions coincide at  $\delta$  1.28). Allylic and nonallylic methylene groups (near  $\delta$  2.5 and 1.5, respectively),  $\alpha$ -carbo-methoxy methine groups ( $\delta$  2.5–3), methoxy groups ( $\delta$  3.6–3.7), and bridgehead methines ( $\delta$  2.4–2.6) all appear. Their presence restricts the structural possibilities to the set **21–24** or an alternative set of double bond position isomers generalized as **25**, which is sufficiently implausible on mechanistic grounds that it need not be considered further.



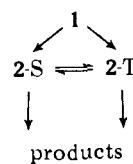
**Variation of the Cycloadduct Composition with Concentration. The Dilution Effect.** Unless proper precautions are observed, the composition of the cycloadduct mixture from the thermal deazetation of **1** in the presence of dimethyl maleate tends to be nonreproducible. Part of the difficulty can be traced to the adventitious presence of oxygen (more fully described later), which has a profound effect on both the absolute yield and the distribution of adducts. A second variable is the concentration of the trapping agent (not the ratio of trapping agent to diazene **1**), which is most easily discerned qualitatively as an increased relative yield of bridged adducts (**16–18**) and of trans fused adducts (**23** and **24**) as the initial concentration of dimethyl maleate is decreased. The dilution effect is reminiscent of the solution phase behavior of some carbenes<sup>22</sup> and nitrenes,<sup>23</sup> which has been rationalized as the result of the initial generation of an unstable, singlet intermediate. This species either is captured in a second-order reaction by the trapping agent or undergoes competitive first-order intersystem crossing to a ground state triplet form.

Anticipating a body of supporting evidence, we show in Scheme II an analogous cascade mechanism for the reactions of diyl **2**. The key features are the stereospecificity and regioselectivity postulated for the reactions of the first-formed

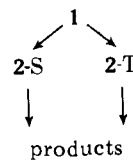
Scheme II. Cascade Mechanism for the Formation and Capture of TMM Intermediates by Dimethyl Maleate ( $\text{X} = \text{CO}_2\text{CH}_3$ )



Scheme III



Scheme IV

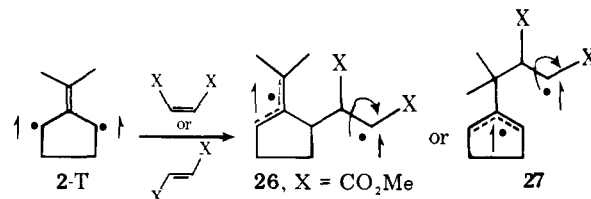


singlet, **2-S**. The preference for syn cycloaddition to olefins ( $k_g \gg k_h$ ) is paralleled by the similar behavior of singlet carbenes and nitrenes,<sup>22,23,27</sup> but the strong bias toward fused (F) rather than bridged (B) adducts ( $k_g \gg k_c$ ) has no counterpart elsewhere and has occupied much of our attention.<sup>24</sup>

Although Scheme II shows no direct pathway from the diazene to the triplet, we note that, in general, the observed dilution effect also would be consistent with a mechanism in which **2-S** and **2-T** in part were formed competitively from **1**, provided a cross-over step  $2\text{-S} \rightarrow 2\text{-T}$  is inserted (Scheme III). The dilution effect rules out a mechanism (Scheme IV) in which **2-S** and **2-T** are formed competitively and simply go on to products. In other words, at least part of the overall process must involve *sequential* formation of two or more capturable intermediates. The first of these is formulated in Scheme II as a true singlet diyl (**2S**), although we leave open the possibility that the actual reactive species may be one of the corresponding bicyclic hydrocarbons, 5-isopropylidenebicyclo[2.1.0]pentane (**6**) or 6,6-dimethylbicyclo[3.1.0]hex-1-ene (**7**).<sup>18,24</sup>

Unimolecular formation of the first capturable intermediate, formulated in Scheme II as **2-S**, must be the rate-determining step for product formation. The overall disappearance of **1** in *o*-dichlorobenzene solution, monitored by NMR spectroscopy, is independent of the concentration of the powerful trapping agent fumaronitrile. The first-order rate constants at 52 °C have values ( $\times 10^4$  s) of 1.7, 1.5, 1.6, and 1.5 with standard deviations of about  $\pm 0.1$  unit, at fumaronitrile concentrations of 0, 0.1, 0.2, and 0.4 M, respectively. These are to be compared with the value 1.8 at 52 °C extrapolated from data obtained on benzene solutions of **1** by a later, more accurate method.<sup>25</sup> The results preclude a bimolecular olefin-diazene reaction as the rate-determining step and are consistent with deazetation of **1** to a capturable intermediate.

The loss of the original *cis* stereochemistry of the trapping agent, dimethyl maleate, in the fused adducts  $t\text{F}_1$  and  $t\text{F}_2$  at low olefin concentration is consistent with an increased contribution to the product from a stepwise reaction of the triplet biradical **2-T**. Formation of the first bond leads to an intermediate, **26** or **27**, in which rotation about the stereochemically



significant bond is competitive with the rate of ring closure. Rotational isomers of these same intermediates could be formed from the trans olefin, dimethyl fumarate, and the amount of the original olefin stereochemistry that survives in the product will depend upon the relative rates of internal rotation and ring closure. As the following analysis will show, the products from reactions at "infinite dilution" of the

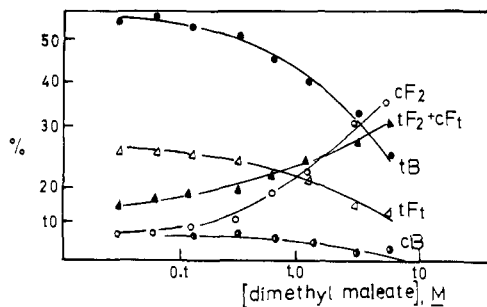


Figure 1. Variation in composition of cycloadduct mixture with olefin concentration in the pyrolysis of diazene **1** with dimethyl maleate at 60 °C in CH<sub>3</sub>CN. The curves for 80 °C are virtually indistinguishable.

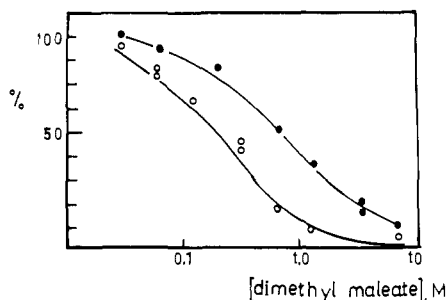


Figure 2. Variation in yield of dimers with olefin concentration in the pyrolysis of diazene **1** with dimethyl maleate at 60 (lower curve) and at 80 °C (upper curve).

trapping agent are almost stereorandomized, as would be expected if the internal rotation were fast.<sup>27</sup>

The dilution effect can be examined quantitatively by pyrolysis of a series of samples containing successive dilutions of a constant molar ratio (1:10) of diazene **1** and dimethyl maleate or dimethyl fumarate. The composition of the product mixture changes in a regular way, as is shown in Figures 1–4, where for convenience the abscissa is plotted logarithmically. With dimethyl maleate, the relative amounts of the cis fused isomers cF<sub>1</sub> and cF<sub>2</sub> decline, while those of both trans fused (tF<sub>1</sub> and tF<sub>2</sub>) and trans bridged (tB) increase (Figure 1). At the same time, the yield of the dimers increases with dilution, from 5% of the products in 6.6 M maleate to almost 90% below 0.1 M (Figure 2). With dimethyl fumarate, the relative amounts of the tF<sub>1</sub> and tF<sub>2</sub> decline, while that of tB increases from about 10% of the cycloadducts at 0.3 M fumarate to about 50% of the total product at fumarate concentrations below 0.01 M (Figure 3). The dilution effect on the dimer yield is much less dramatic with fumarate than with maleate (Figure 4). Even at the low fumarate concentration of 0.01 M, only about 5% of dimer is formed.

A few experimental matters deserve mention here. The absolute yields of dimers plus cycloadducts, as determined gas chromatographically with diphenyl ether internal standard, are quantitative within the experimental error of about 1–2%, and all peaks in the chromatogram can be identified. The composition of any given cycloadduct mixture is reproducible to better than 0.5% in each component. It is necessary to use carefully purified, fumarate-free dimethyl maleate, because fumarate is much more reactive than maleate. This can be inferred already from the difference in the dilution effect on the dimer yield. The dimers represent that portion of the TMM species which eludes capture by the trapping agent (Scheme II), and the much higher dimer yield from maleate (at a specific concentration) than from fumarate suggests that fumarate is the more efficient TMM trap. The relative rates can be deduced quantitatively, as we shall see, but the use of ordinary dimethyl maleate, which may contain about 1% of fumarate,

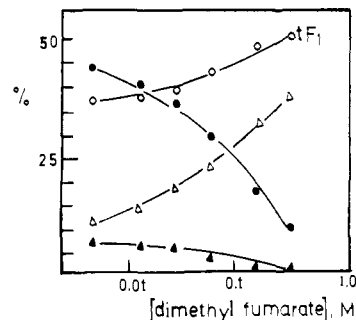


Figure 3. Variation in composition of cycloadduct mixture with olefin concentration in the pyrolysis of diazene **1** with dimethyl fumarate at 60 °C in CH<sub>3</sub>CN.

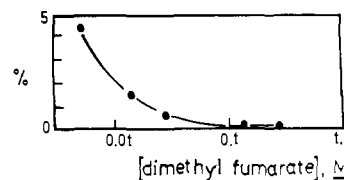
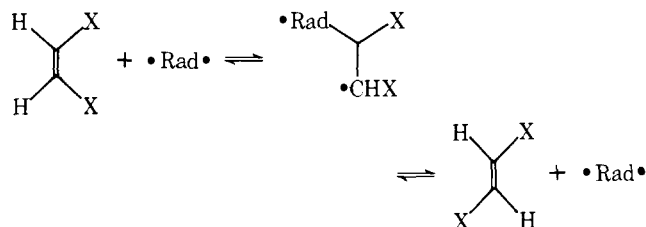


Figure 4. Variation in total yield of dimers 8–11 in the pyrolysis of diazene **1** and dimethyl fumarate in CH<sub>3</sub>CN at 60 °C.

can give misleading results, because the reactivity ratio will cause a disproportionately large amount of the product to originate from TMM–fumarate combinations.

This difficulty also must be taken into account even if the reactions use pure maleate, because of the possibility that the first step of the triplet cycloaddition might be reversible, which could cause geometric isomerization of the starting olefin concurrent with cycloaddition, viz.



Although we recover either starting olefin unchanged from the reaction mixtures, in the case of maleate reactant, this again is not definitive because the differential reactivity would tend to drain off any small amount of fumarate formed. However, the dilution curves themselves contain evidence that this worrisome isomerization does not affect the product composition. Thus, the ratios of two of the cycloadduct isomers, tF<sub>1</sub> and tB, from reaction with fumarate and maleate behave differently. With maleate, the ratio is constant at 0.45 ± 0.01 throughout the range of olefin concentrations studied (6.6–0.33 M), whereas with fumarate, it varies from 5.2 at 0.34 M olefin to 0.83 at 0.007 M olefin. Therefore, the trans products formed in the maleate reaction cannot have come from those amounts formed by isomerization, or this product ratio should have shown at least part of the concentration dependence observed with pure fumarate. We may conclude that the loss of stereochemistry in the products from the maleate reaction is solely due to a mechanism characteristic of the cycloaddition itself, for example, to rotational isomerization of the biradical adduct intermediate **26** or **27** before ring closure.

As Figure 2 shows, at a given concentration of trapping agent, the yield of dimers is higher at higher reaction temperature. We attribute this effect to the increased rate of decomposition of the diazene **1** at higher temperature, which results in a higher steady-state concentration of diyl **2**. Since

cycloadduct formation is first order in diyl, but dimer formation is second order, the higher diyl concentration would favor dimerization.

**Evidence for Two and Only Two Product-Forming Intermediates.** A cascade mechanism with two intermediates, such as that of Scheme II, makes some testable predictions about the mutual dependence of the yields of the various products, I, J, K, . . . , etc. The observed fraction ( $P_i$ ) of any one product (I) may be expressed as a weighted sum of the fractions of that product formed from each of the two intermediates, as is expressed in eq 1, where  $I_S$  and  $I_T$  are fractions of the total singlet-derived and total triplet-derived adducts that are I, and  $X_S$  and  $X_T$  are the fractions of singlet-derived and triplet-derived total product.

$$P_i = X_S I_S + X_T I_T \quad (1)$$

At any one temperature, the fractions  $I_S$  and  $I_T$  are constants, whereas the fractions  $X_S$  and  $X_T$  vary with the conditions of the reaction, especially with the concentrations of trapping agent and oxygen.

The relationship between any two product fractions,  $P_i$  and  $P_j$ , is given by eq 2,

$$\frac{P_j}{P_i} = \frac{X_S J_S + X_T J_T}{X_S I_S + X_T I_T} \quad (2)$$

which can be shown to correspond to a linear relationship of  $P_j$  and  $P_i$ . Note that  $X_S + X_T = 1$ ,  $0 \leq I_S + I_T \leq 2$ ,  $I_S + J_S + K_S + \dots = 1$ , and  $I_T + J_T + K_T + \dots = 1$ .

Using these relationships, we may express  $P_j$  and  $P_i$  as in eq 3 and 4.

$$P_j = (J_T - J_S)X_T + J_S \quad (3)$$

$$P_i = (I_T - I_S)X_T + I_S \quad (4)$$

The terms  $I_S$ ,  $J_S$ ,  $I_T$ , and  $J_T$  are constants representing the distribution of products from each intermediate. For example,  $I_S/J_S$  is the ratio of rate constants that controls the formation of products I and J from intermediate S. In eq 3 and 4,  $P_i$  and  $P_j$  both appear as linearly dependent on the variable  $X_T$ , the fraction of total product from the second intermediate T. The value of  $X_T$  decreases as the concentration of the trapping agent increases. Since both  $P_j$  and  $P_i$  are linear functions of  $X_T$ , they must be linear functions of each other. Combining eq 3 and 4, we get eq 5, which explicitly shows  $P_j$  to be linear in  $P_i$ .

$$P_j = \left[ \frac{J_T - J_S}{I_T - I_S} \right] P_i - \left[ \frac{J_T - J_S}{I_T - I_S} \right] I_S + J_S \quad (5)$$

Among the interesting special cases is the one in which both products I and J come from a single intermediate, say T. Under these constraints,  $I_S = J_S = 0$ , and eq 5 takes the limiting form:

$$P_j = (J_T/I_T)P_i \quad (6)$$

which corresponds to a linear graph with a zero intercept. In the case where reference compound I comes only from T ( $I_S = 0$ ,  $J_S = 1$ ) and I and J are the only products ( $J_T + I_T = 1$ ), eq 5 becomes eq 7, which has a slope of  $-1$  and an intercept of 1.

$$P_j = -P_i + 1 \quad (7)$$

A related special case occurs when two or more additional products ( $J$ ,  $K$ , . . . , etc.) come from both intermediates, but the reference product I comes only from T. Thus,  $J_T + K_T + \dots + I_T = 1$  and  $J_S + K_S + \dots = 1$ . A plot of the sum of  $J + K + \dots$  vs.  $P_i$  will be represented by eq 8 and 9, which like eq 7 show a slope of  $-1$  and an intercept of 1.

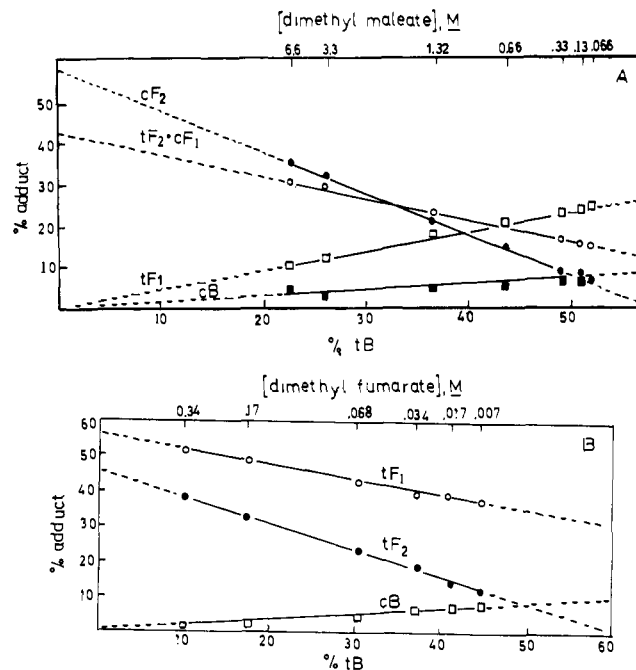


Figure 5. Least-squares fit to linear form of the percent of various adducts as a function of trans-bridged adduct (tB) in the pyrolysis of diazene 1 at varying concentrations of dimethyl maleate (A) and dimethyl fumarate (B) in  $\text{CH}_3\text{CN}$  at  $60^\circ\text{C}$ .

$$P_j + P_k + \dots = (1/I_T)[(J_T + K_T + \dots) - (J_S + K_S + \dots)]P_i + J_S + K_S + \dots \quad (8)$$

$$P_j + P_k + \dots = -P_i + 1 \quad (9)$$

This analysis suggests that a simple test for the number of product-forming intermediates involved in the dilution effect would consist of a plot in which the abscissa of each point is the relative percentage of one adduct formed, and the ordinate is the relative percentage of another adduct formed at the same olefin concentration. The plot should be linear for a two-intermediate mechanism. If three or more intermediates were involved, linearity could occur accidentally for a pair of products but would be unlikely for all pairs.

In practice, regraphing the data of Figures 1 and 3 with percent tB as the abscissa provides the most sensitive test of the hypothesis since the variation of this product covers the largest range. The graphs of Figure 5 are all linear with correlation coefficients  $>0.99$  for the least-squares regression line shown. For the purpose of confirming the two-intermediate mechanism, the plots of Figure 5 have the desirable feature of being independent of an accurate value for the absolute concentration of the trapping olefin.

In both systems, there are products whose plots extrapolate to the origin. These are  $tF_1$  and  $cB$  from maleate and  $cB$  from fumarate. These must be the adducts that are formed together with tB from a single common intermediate. The fact that in each system the stereochemical relationship of the carbomethoxy groups in one of these "zero-intercept" adducts is the inverse of that in the olefin supports the presumption that the intermediate is the triplet biradical 2-T.

The limiting value of the product composition that corresponds to a "pure singlet" source for all of the products lies somewhere between the highest (leftmost) concentration point and the origin. The composition of the product from the spin-equilibrated, triplet-enriched mixture of intermediates lies somewhere between the lowest (rightmost) concentration point and the first intersection of a line of negative slope with the abscissa. In the maleate system, the limiting singlet composi-

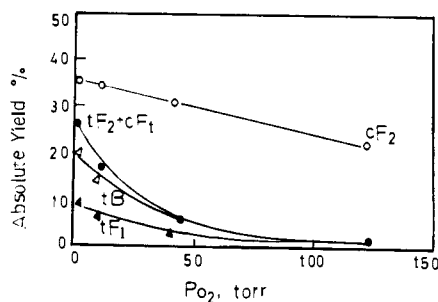


Figure 6. Variation with oxygen pressure of composition of product mixture in the pyrolysis of diazene **1** in neat dimethyl maleate at 60 °C.

Table I. Limiting Product Compositions in the Reactions at 60 °C of Olefins with **1** as Determined by Extrapolation to Infinite Dilution

solvent	adduct				
	tF <sub>1</sub>	tB	tF <sub>2</sub> + cF <sub>1</sub>	cF <sub>2</sub>	cB
from maleate					
C <sub>6</sub> H <sub>6</sub> or PhCH <sub>3</sub>	20	60	11.5	3	6
<i>i</i> -PrOH	22	54.5	12.5	4	6
CH <sub>3</sub> CN	23.5	52.5	13.5	5.5	6
from fumarate					
CH <sub>3</sub> CN	35.5	45.8	10.0	~0.1	7.6

tion is 31–41% tF<sub>2</sub> + cF<sub>1</sub> and 35–56% cF<sub>2</sub>. The limiting triplet composition is about 7% cB, 10–12% tF<sub>2</sub> + cF<sub>1</sub>, 25–28% tF<sub>1</sub>, and 44–57% tB. These triplet values agree (Table I) with those obtained by mere extrapolation of a plot of percent of each adduct vs. olefin concentration to infinite dilution in CH<sub>3</sub>CN. In the fumarate case, the singlet composition is 40–45% tF<sub>2</sub> and 52–56% tF<sub>1</sub>, whereas the triplet composition (compare Table I) is about 7–10% cB, 38–45% tF<sub>1</sub>, and 44–60% tB. The ranges for the singlet compositions are limits imposed by the pairwise plots and can be narrowed to give more precise values by the methods to be described.

**Solvent Effects.** The effect of solvent polarity on the product composition is small.<sup>26</sup> However, heavy-atom solvents seem to cause some suggestive trends. In the addition of dimethyl maleate, for example, if spin-orbit coupling were to cause a major increase in the rate of intersystem crossing of the singlet biradical, the ratio of adduct cF<sub>2</sub> (derived mostly from the singlet) and tB (derived mostly from the triplet) should decline sharply as the atomic number of the solvent heavy atom increases. For the series chlorobenzene, bromobenzene, iodobenzene, the cF<sub>2</sub>:tB ratios at 2.0 M dimethyl maleate are 0.71, 0.59, and 0.44, respectively, whereas by contrast the ratio tF<sub>1</sub>:tB (both adducts being largely triplet-derived) hardly changes (0.34, 0.37, 0.37). The decline in the cF<sub>2</sub>:tB ratio is small. Even in iodobenzene, the value 0.41 found under these conditions is well above the limiting “spin-equilibrated” value of about 0.1 shown in Table I. We therefore cannot exclude the possibility that the trend of the data in halogenated solvents has another cause, but the direction and magnitude of the effect are consistent with a weak heavy-atom facilitation of spin inversion.

**Effect of Molecular Oxygen.** In the reactions of carbenes with olefins, admission of oxygen to the reaction mixture frequently increases the stereospecificity of the cycloaddition, presumably because oxygen selectively scavenges the triplet. We observe a similar effect in the reactions of the diyl **2**. Figure 6 shows that, in the reaction with neat dimethyl maleate, the absolute yield of the singlet product cF<sub>2</sub> declines only moderately as the oxygen pressure increases, but those of the triplet products, tB, tF<sub>2</sub>, and tF<sub>1</sub>, decrease sharply to values of 1–2%.

Table II. Composition of Product Mixtures from Pyrolysis of Diazene **1** in the Presence of Dimethyl Maleate (DMM) at 250 Torr of Oxygen (60 °C, CH<sub>3</sub>CN Solvent)

[DMM], M	% adduct					absolute yield adduct dimer	
	tF <sub>1</sub>	tB	cF <sub>1</sub>	cF <sub>2</sub>	cB		
6.6 <sup>a</sup>	1.7	1.4	41.3	54.6	1.0	54	8
3.3 <sup>b,c</sup>	2.2	1.5	44.3	50.4	1.7	32	9
1.3 <sup>b,c</sup>	4.3	4.8	43.6	45.2	2.0	17	10
0.66 <sup>b,c</sup>	5.4	9.2	39.4	46.0		15	4

<sup>a</sup> Neat. <sup>b</sup> In CH<sub>3</sub>CN. <sup>c</sup> Nominal concentration, not corrected for solvent vaporization.

Table III. Composition of Product Mixtures from Pyrolysis of Diazene **1** in the Presence of Dimethyl Fumarate (DMF) at 250 Torr of Oxygen (60 °C, CH<sub>3</sub>CN Solvent)

[DMF], <sup>b</sup> M	% adduct					abs yield of adduct <sup>a</sup>
	tF <sub>1</sub>	tF <sub>2</sub>	tB	cF <sub>2</sub>		
0.298	55.8	42.5	1.5	0		62.4
0.224	56.3	42.8	1.0	0		55.9
0.149	56.4	43.1	1.2	0		45.4
0.075	56.3	42.5	1.2	0		29.4
0.037	56.2	42.4	1.4			17.8
av:	56.2	42.7	1.3	0		
± σ	0.2	0.3	0.2	0		

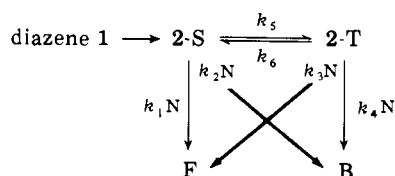
<sup>a</sup> Dimers of diyl **2** are absent (<1%) under these conditions. <sup>b</sup> Nominal concentration, not corrected for solvent vaporization.

This suggests that, at high enough concentration of dimethyl maleate, 100–150 Torr of oxygen pressure suffices to capture nearly all of the triplet intermediates. The total yield of cycloadducts also declines, which is readily understood if the diyl **2** is being consumed in a competitive reaction with oxygen.<sup>28</sup> It is not clear whether some singlet **2** also reacts with oxygen, either directly or by a singlet → triplet diyl spin-inversion induced by the paramagnetism of oxygen, but, at a minimum, it seems certain that the reaction of oxygen with **2-T** is much faster than with **2-S**.

The product composition at the highest oxygen pressure in neat dimethyl maleate represents our closest experimental approach to the limiting “pure singlet” composition. It seems likely, however, that even the small amounts of trans products observed under these conditions are not authentic **2-S** + dimethyl maleate cycloadducts. In part, they could arise from the small amount (~0.1%) of dimethyl fumarate present in the maleate reactant since the 60-fold greater reactivity of fumarate toward **2-S**<sup>18c,29</sup> would lead to a disproportionately large trans component in the reaction mixture from maleate. Moreover, the low reactivity of maleate toward the singlet<sup>18c,29</sup> apparently allows some of the **2-S** intermediate to escape capture and undergo intersystem crossing. Table II shows that the contribution of trans and bridged products in the maleate system increases detectably upon modest dilution, even at 250 Torr of oxygen pressure. We conclude that the “pure singlet” composition from maleate is almost completely stereospecific for syn and regiospecific for fused products.

With the more reactive fumarate (Table III), the same pressure of oxygen, 250 Torr, suffices to keep the product composition invariant with dilution, even over an olefin-free concentration range that causes large changes in the oxygen-free system (Figure 3). The average composition shown in Table III therefore may be accepted as the “pure singlet” value. Again, singlet cycloaddition is stereospecifically syn. The regiospecificity also is high, but there is no reason to doubt that the 1.3 ± 0.2% of tB product is really of singlet provenance. We conclude that the regiospecificity, expressed as *F/B*, the ratio of total fused to bridged product, is 98.7/1.3, or 76.

Scheme V



**Ratio of the Singlet Capture and Intersystem Crossing Rate Constants.** When the concentration and reactivity of the trapping olefin, N, are sufficiently high to prevent appreciable dimer formation, the cascade mechanism of Scheme II may be written as Scheme V, which by way of the steady-state assumption applied to the biradicals 2-S and 2-T gives the expression eq 10 for the ratio of fused to bridged cycloadducts

$$(F/B) = \frac{k_3k_5 + k_1\{k_6 + (k_3 + k_4)[N]\}}{k_4k_5 + k_2\{k_6 + (k_3 + k_4)[N]\}} \quad (10)$$

( $F/B$ ) as a function of  $[N]$ . This boundary condition is met in all but the most dilute reactions of diy1 2 with dimethyl fumarate. From the very large ( $F/B$ ) ratio in the oxygenated and high concentration runs, we know that  $k_2$ , the rate constant for production of bridged product from 2-S, must be small. If we make the approximation  $k_2 \sim 0$ , we obtain eq 11, which predicts that the ( $F/B$ ) ratio should be linear in  $[N]$  and have an intercept,  $k_3/k_4$ , which is the ( $F/B$ ) product distribution ratio from the second intermediate 2-T.

$$(F/B) \cong (k_1/k_5)\{(k_6/k_4) + (k_3/k_4) + 1\}[N] + (k_3/k_4) \quad (11)$$

If the singlet-triplet gap is large enough so that the rate of triplet  $\rightarrow$  singlet reversion ( $k_6$ ) is a small fraction of the trapping rate constant  $k_3$ , eq 11 becomes eq 12.

$$(F/B) \cong (k_1/k_5)\{(k_3/k_4) + 1\}[N] + k_3/k_4 \quad (12)$$

The slope of the ( $F/B$ ) vs.  $[N]$  plot divided by the term  $1 + (k_3/k_4)$  thus is either equal to (eq 12) or an upper limit of (eq 11)  $k_1/k_5$ , the ratio of the rate constants that control the disposal of the singlet 2-S between capture and intersystem crossing.

Figure 7 shows this plot for the pyrolytic generation of diy1 2 from diazene 1 in acetonitrile solutions of dimethyl fumarate. In contrast to the plots of Figure 5, where linearity was not dependent on accurate knowledge of the olefin concentrations, Figure 7 requires such information. Because of difficulties (see Experimental Section) in the specification of the sample volumes at the reaction temperature (60 °C), the data at high fumarate concentrations are less reliable than elsewhere. The points conform to a linear graph ( $r = 0.998$ ) with a slope of 15.1 and an intercept of 0.89. If the boundary conditions of eq 12 apply ( $k_6/k_3 \sim 0$ ), these parameters may be interpreted as  $k_3/k_4 = 0.89$  and  $k_1/k_5 = 8.0 \text{ M}^{-1}$ .

As an independent check on the applicability of eq 12, we can use another procedure to calculate  $k_1/k_5$ . The ratio of the sum of singlet-derived products to the sum of triplet-derived products  $X_S/X_T$  as a linear function of olefin concentration  $[N]$  is given by eq 13.

$$X_S/X_T = \frac{k_6(k_1 + k_2)}{k_5(k_3 + k_4)} + \frac{(k_1 + k_2)[N]}{k_5} \quad (13)$$

As already has been shown,  $k_2 \sim 0$ , and if  $(k_6/k_3) \sim 0$ , this function becomes eq 14. A plot of the singlet-triplet product ratio against olefin concentration should go through the origin and should have a slope equal to  $k_1/k_5$ .

$$X_S/X_T = (k_1/k_5)[N] = X_S/(1 - X_S) \quad (14)$$

The percent of triplet and singlet products can be calculated from eq 15, which is derived from the limiting values of product

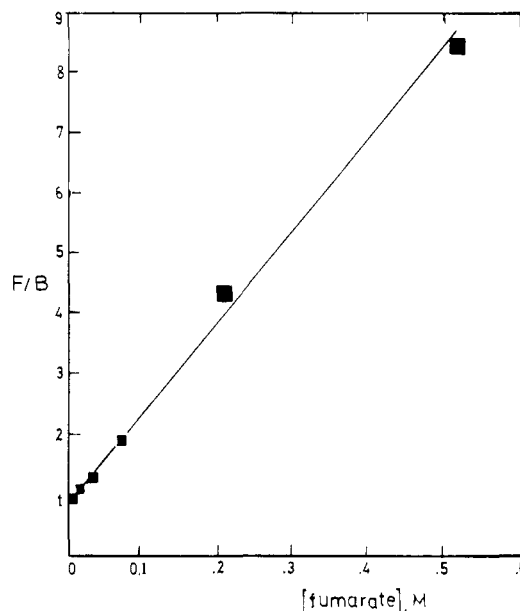


Figure 7. Ratio of fused to bridged adducts as a function of the concentration of dimethyl fumarate in  $\text{CH}_3\text{CN}$ , 60 °C. The experimental error is indicated by the size of the data point rectangles.

$$\%T = 100(\%tB_{\text{obsd}} - 1.3)/(46 - 1.3) \quad (15)$$

tB, 46% from the "pure triplet" extrapolation (Table I), and 1.3% from the "pure singlet" (Table III). A plot (not shown) of the ratio  $X_S/X_T$  against the concentration of dimethyl fumarate is linear ( $r = 0.9997$ ), with an intercept of 0.002 and a slope of  $8.3 \text{ M}^{-1}$ . This value of  $k_1/k_5$  is in good agreement with the value deduced above.

As a further check on  $k_1/k_5$ , we note that a plot of any product percentage vs. the fraction of the total product that is singlet derived should be linear. By using various trial values of  $k_1/k_5$  and the experimental values of the fumarate concentration, we can generate from eq 14 a series of values for the fractions of singlet product at each experimental concentration. If  $k_1/k_5$  is incorrectly chosen, the plot of the experimental value for adduct I vs.  $X_S/X_T$  will deviate from linearity, and the "best value" may be found by trial and error as the one that maximizes the correlation coefficient ( $r$ ). This procedure applied to tB, tF<sub>2</sub>, and tF<sub>1</sub> gives  $k_1/k_5$  values ( $\times \text{M}$ ) of 7.0 ( $r = 0.9996$ ), 8.0 ( $r = 0.9996$ ), and 7.0 ( $r = 0.9997$ ). These values are in reasonable agreement with those obtained by the earlier methods of treating the data and suggest that the actual value of  $k_1/k_5$  is about  $7.7 \pm 0.5 \text{ M}^{-1}$ .

A final check on the internal consistency of the  $k_1/k_5$  value with the experimental data comes from transforming eq 14 to the form of eq 16, where  $R = k_1/k_5$ . Using the value  $R = 7.7$

$$X_S = R[N]/(R[N] + 1) \quad (16)$$

$\text{M}^{-1}$  and the definition  $X_S + X_T = 1$ , we may calculate the fraction of singlet- and triplet-derived product at any concentration of fumarate,  $[N]$ . Combining these fractions ( $X_S$  and  $X_T$ ) with the limiting singlet and triplet product distributions (Tables I and III), we may use eq 1 to calculate the product distribution at any  $[N]$ . As Figure 8 shows, the experimental data fit the curves calculated from  $R = 7.7 \text{ M}^{-1}$  quite well.

A following paper<sup>29</sup> deduces ratios of capture and intersystem crossing for the singlet diy1 2 in reactions with other trapping agents. In combination with the present result, these ratios form the basis for a ranking of relative diylphilicities of olefins.



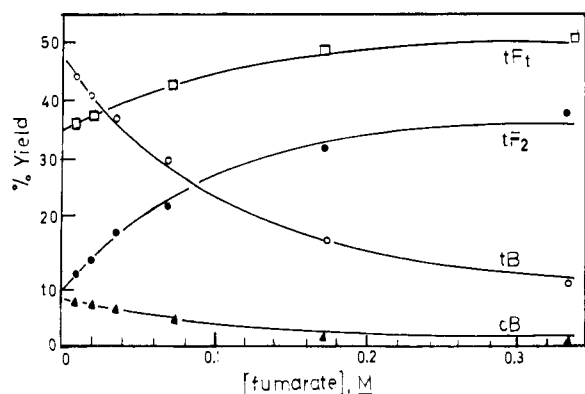


Figure 8. Experimental (points) and calculated (curves) variation of cycloadduct yield with concentration of dimethyl fumarate in the pyrolysis of diazene **1** at 60 °C. The curves are calculated by using  $7.7 \text{ l M}^{-1}$  as the ratio of singlet capture to intersystem crossing ( $k_1/k_5$ ).

### Experimental Section

**Instruments.** Nuclear magnetic resonance (NMR) spectra were taken on Varian A-60 or Jeolco Minimar-100 spectrometers in carbon tetrachloride or deuteriochloroform solutions as specified. Chemical shifts were measured on the recorded spectrum with reference to tetramethylsilane ( $\text{Me}_4\text{Si}$ ) and are recorded as follows: chemical shift  $\delta$  (parts per million downfield from  $\text{Me}_4\text{Si}$ ), multiplicity, number of protons, coupling constant, assignment. Infrared (IR) spectra were recorded on a Perkin-Elmer 237 spectrometer, usually in carbon tetrachloride solution with carbon tetrachloride as reference. Ultraviolet spectra were recorded on a Shimadzu-Bausch and Lomb Spectronic 200.

Mass spectra were recorded on a Hitachi Perkin-Elmer RMU-6 single-focusing instrument. Preparative gas chromatography (GC) was performed on a Varian Aerograph 90-P-3 using columns indicated below. GC analysis was performed on a Perkin-Elmer Model 900 gas chromatograph using  $1/8$ -in. packed or  $1/16$ -in. capillary columns (see Table IV) and a flame ionization detector. Melting points were taken using a Fisher-Johns block or a Thomas-Hoover apparatus and are uncorrected.

GC peak integrals were recorded with a Hewlett-Packard 3700 A digital integrator. In cases of severely drifting base line, an assumed base line was sketched and a Xerox copy of the chromatogram was cut out and weighed. Since duplicates proved to be reproducible within 0.3%, a single weighing was ordinarily considered sufficiently accurate.

Calculations were done on a Hewlett-Packard 3100 programmable calculator. We thank Dr. Richard Vickers for a copy of his least-squares program which gives the standard deviation of the slope and intercept.

Chemicals used were generally reagent grade. Special purification techniques, especially for halogenated solvents, are noted where appropriate. Solvents were not dried or distilled before use, unless noted.

**Standard Procedures.** Pyrolysis tubes were made from 7-mm Pyrex tubing cut into open 30-cm lengths, which were placed in a large chromatography column and washed successively with chromium oxide-sulfuric acid cleaning solution, water, dilute aqueous ammonia, and flowing water for an hour or more, and air dried. The open tubes were parted in the middle with a flame to form two sample tubes.

Stock solutions were made up by weighing components to  $\pm 0.1 \text{ mg}$  on a Mettler H20T balance, and adding solvent in a 1- or 2-mL volumetric flask in the case of dimethyl fumarate. The stock solution was measured into the sample tube with a microsyringe, and the solvent was added with a microsyringe or pipet. Hamilton syringes of capacity 10, 50, and 500  $\mu\text{L}$  were used. The sample tubes were centrifuged briefly to drive all solution to the bottom and immediately degassed in a vacuum line or, in the case of oxygenated samples, sealed on the apparatus described below.

Samples were degassed on a vacuum line capable of maintaining 0.1–0.01  $\mu\text{mHg}$ . It was found useful for this purpose to employ a special "cow". This was a conical manifold made from a 500-mL Erlenmeyer flask with a ground joint fitting into the working manifold

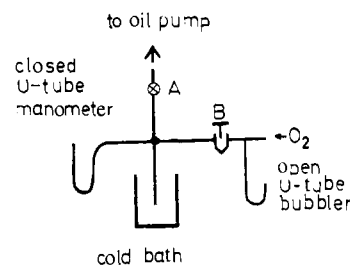


Figure 9. Diagram of apparatus for introducing oxygen atmosphere into sample tubes.

Table IV. GC Columns Used

A	5 ft $\times$ $1/8$ in. 1% Carbowax 20 M on 100–200 mesh silanized Chromosorb P
B	5 ft $\times$ $1/8$ in. 5% triscyanoethoxypropane on 100–120 mesh silanized Chromosorb P
C	200 ft $\times$ $1/16$ in. Carbowax 20 M capillary
D	100 ft $\times$ $1/16$ in. XE-60 cyanosilicone capillary
E	20 ft $\times$ $3/8$ in. 20% FFAP on 60–80 Chromosorb P

at the top. On the bottom were sealed six high-vacuum cup stopcocks terminating in 10–30 mm standard taper joints. Six sample tubes were attached to these joints with 0.25-in. poly(vinyl chloride) tubing and immersed in sufficient liquid nitrogen to cover the liquid samples. After a minute or so to condense all vapor, the stopcocks were opened to vacuum. Use of oxidation-resistant silicone diffusion pump oil permitted direct evacuation through the diffusion pump instead of pumping down with the forepump.

When a satisfactory vacuum was attained, the stopcocks on the "cow" were closed and the sample tubes allowed to warm. Care was necessary to prevent too rapid warming, which led to rapid evolution of gas and bumping of sample. When all the liquid had thawed, the freezing, pumping, and thawing steps were repeated once or twice. Finally, the tube was frozen and evacuated, the stopcocks were closed, and the tube was carefully sealed with an oxygen-gas flame.

When the sample tube was to be filled with oxygen, the apparatus depicted schematically in Figure 9 was used. The sample tube was inserted in a single or multiple tube holder and chilled in a bath of dry ice and methylene chloride or, better, 1,1,1-trichloroethane. The tube was evacuated roughly, stopcock A closed, and needle valve B opened slowly. This cycle was repeated twice, the last time adjusting the pressure to the desired value (e.g., 200 Torr) while observing the manometer. The tube was then sealed. The vapor over such a bath will not ordinarily ignite even when a flame is played over it, but the flame should not come in contact with liquid adhering to the tubes.

Pyrolyses were run in an oil bath, usually at  $60 \pm 2$  °C, although a few were run at higher temperatures. Precise temperature control was not considered necessary since the cycloadduct composition appeared to be relatively insensitive to temperature. However, the amount of dimer formed (in the reaction with dimethyl maleate, in particular) was moderately sensitive to the decomposition rate.

**Retention Times of Adducts.** Since a GC column was sometimes used at a lower temperature or flow rate as its resolution deteriorated, no single set of retention times could be used for reference. However, since several isomers were present in each reaction mixture, there was rarely any question of the identities of the peaks, once the relative retention times of each isomer had been established. In comparing sets of different retention times from different columns at the same temperature, better agreement was found when the retention times (Table V), rather than the adjusted retention times (retention time minus dead time, i.e., time for passage of carrier from injector to detector), were multiplied by a constant factor.

**7-Isopropylidene-2,3-diazabicyclo[2.2.1]hept-2-ene, 1.** *N,N*-Dicarbomethoxy-2,3-diaza-7-isopropylidenebicyclo[2.2.1]heptane<sup>30</sup> (15.8 g) was dissolved in 30 mL of degassed ethylene glycol. This was added rapidly under nitrogen with vigorous stirring to a 125 °C solution of 41.9 g of KOH and 60 mL of degassed ethylene glycol in a 250-mL flask. The mixture was stirred under nitrogen at 125 °C for 30 min, then cooled to room temperature. Sodium bicarbonate (20 g) was added, and the mixture was stirred for 30 min. The suspension

**Table V.** Retention Times of Diester Adducts (Minutes)<sup>a</sup>

compd	retention time	
	A	B
dimer	1.9	
dimer	2.2	
Ph <sub>2</sub> O	4.3	
tF <sub>1</sub>	8.2	33.5
tB	9.0	33.5
tF <sub>2</sub>	9.8	38.2
cF <sub>1</sub>	9.8	43.2
cxB	9.8	50.4
cF <sub>2</sub>	11.4	57.3
cnB	15.3	60.3

<sup>a</sup> Conditions: Perkin-Elmer 900 analytical gas chromatograph. (A) Column A (Carbowax): oven 150 °C, injector 180 °C, manifold 200 °C, nitrogen carrier 50 psi regulated to rotameter setting 2. (B) Column B (TCEP): oven 125 °C, injector 180 °C, manifold 200 °C, nitrogen carrier 50 psi regulated to rotameter setting 4.

was filtered, and a little alcohol was used to wash the solid material. Yellow mercuric oxide (36 g) was added to the mixture, which was stirred for 1–2 h at 0 °C. The viscous mixture was filtered through Celite in a coarse fritted-glass funnel. The ethylene glycol layer was washed with ether (5 × 150 mL) and discarded. Most of the ether was removed at reduced pressure at 0 °C. The resulting ether–ethylene glycol mixture was extracted with pentane (4 × 25 mL). The pentane extracts were concentrated at reduced pressure and cooled to –20 °C. The colorless crystals of azo compound that separated were collected at low temperature. Two additional crops were collected by removing more pentane and cooling. The total yield was 4.8 g (57%): NMR (CDCl<sub>3</sub>) δ 1.63 (s, 6, isopropylidene), 1.0–1.7 (m, 4, methylene), 5.37 (bq, 2, bridgehead); UV<sub>max</sub> 340 (ε 65) and 332 nm (62); mp 59–60 °C (dec). The material gave essentially quantitative yields of N<sub>2</sub> upon solution-phase pyrolysis, but partial decomposition in transit precluded a satisfactory combustion analysis. A single-crystal X-ray analysis<sup>31</sup> confirmed the structure.

**Dimethyl Maleate.** Maleic anhydride (50 g) recrystallized from chloroform, 100 mL of methanol, and 1 mL of sulfuric acid were refluxed for 24 h in a Soxhlet extractor with a thimble containing 4A molecular sieves. The methanol was removed on a rotary evaporator, and the remaining liquid was washed with sodium bicarbonate solution, dried (MgSO<sub>4</sub>), and distilled, bp 63–64 °C (2 mm): NMR (neat, external Me<sub>4</sub>Si); δ 3.40 (s, 6, carbomethoxy), 6.01 ppm (s, 2, vinyl).

GC analysis showed about 0.7% of dimethyl fumarate and 0.5% of maleic anhydride. When necessary for quantitative measurements, these impurities were reduced to about 0.1% by preparative GC, using column E at 200 °C.

**Dimethyl Fumarate.** Fumaric acid (50 g), 100 mL of methanol, and 1 mL of sulfuric acid were refluxed for 24 h in the apparatus used for dimethyl maleate synthesis. Solid was present in the flask throughout the reaction. On cooling, the solution solidified. A single recrystallization from chloroform gave neutral dimethyl fumarate, 99.99% pure by GC: NMR (CDCl<sub>3</sub>) δ 3.80 (s, 6, carbomethoxy), 6.83 ppm (s, 2, vinyl).

**Reaction of Diazene 1 and Dimethyl Maleate.** Azo compound 1 (0.5 g) was dissolved in 5 mL of dimethyl maleate and the solution was kept at 60 °C for 8 h. The mixture was concentrated to 1.5 mL by vacuum distillation and the adducts were separated by preparative GC on column E at 200 °C.

Anal. Calcd for C<sub>14</sub>H<sub>20</sub>O<sub>4</sub>: C, 66.65; H, 7.99. Found (for cF<sub>1</sub>): C, 66.37; H, 7.95. For cF<sub>2</sub>: C, 65.89; H, 7.99.

**Reaction of Diazene 1 and Dimethyl Fumarate.** Azo compound 1 (0.5 g) and 5 g of dimethyl fumarate were dissolved in 30 mL of methyl acetate with warming. The solution was refluxed for 8 h. The solution was cooled to 0 °C and the precipitate of dimethyl fumarate separated on a Buchner funnel. The adducts were separated under the same conditions as used for the dimethyl maleate adducts.

Anal. Calcd for C<sub>14</sub>H<sub>20</sub>O<sub>4</sub>: C, 66.65; H, 7.99. Found (for tF<sub>1</sub>): C, 66.80; H, 7.96.

**Reaction of Diazene 1 and Maleic Anhydride.** Azo compound 1 (0.45 g) and 5 g of maleic anhydride were mixed and held at 60 °C under nitrogen overnight. The dark brown melt was poured into a

**Table VI.** Relative Yields (%) of Diester Cycloadducts<sup>a</sup>

olefin	cycloadduct <sup>b</sup>						
	tF <sub>1</sub>	tF <sub>2</sub>	tB	cF <sub>1</sub>	cF <sub>2</sub>	cnB	cxB
dimethyl maleate	9	4	22	26	35	4	0
dimethyl fumarate	51	38	10	0	0	~1	0
maleic anhydride <sup>c</sup>	2	0	1	37	47	1	12

<sup>a</sup> Experimental conditions: temperature 60 °C, reaction time 8 h. Dimethyl maleate 6.6 M, azo compound 0.66 M. Dimethyl fumarate 0.35 M, azo compound 0.035 M in acetonitrile. Maleic anhydride 11 M, azo compound 1.1 M. <sup>b</sup> For abbreviations, see text. <sup>c</sup> The anhydride adducts were allowed to react successively with methanol and diazomethane to form diesters.

sublimator and most of the excess maleic anhydride was sublimed off. The residue was dissolved in methanol and refluxed for 1 h. After removal of methanol on a rotary evaporator, the residue was taken up in ether and esterified with diazomethane.

GC analysis of the three reaction mixtures on column A at 150 °C showed the mixture of diesters given in Table VI. The NMR spectral data are given in Table VII.

**7-Isopropylidenebicyclo[2.2.1]hept-5-ene-2,3-cis-exo-dicarboxylic Anhydride 14.**<sup>21</sup> A solution of 2.5 g of dimethylfulvene and 2.5 g of maleic anhydride in 25 mL of benzene was refluxed for 1 h. The solvent was removed on a rotary evaporator and the residue was recrystallized from ethyl acetate, giving large crystals: mp 136–138 °C (lit.<sup>21</sup> mp 137 °C); NMR (CDCl<sub>3</sub>) δ 1.58 (s, 6, isopropylidene), 3.04 (s, 2, α to carbonyl), 3.89 (t, 2, J = 1.7–2 Hz, bridgehead), 6.46 (t, 2, J = 1.7–2 Hz, vinyl).

**7-Isopropylidenebicyclo[2.2.1]hept-5-ene-2,3-cis-endo-dicarboxylic Anhydride 15.**<sup>21</sup> Dimethylfulvene (8.8 g) was added to a suspension of 8.8 g of maleic anhydride in 80 mL of 0 °C ether, and the mixture was left at 0 °C overnight. On scratching the flask containing the clear yellow solution, exo adduct precipitated (3.9 g). Evaporation of the ether and recrystallization gave 5.8 g of a mixture of endo and exo adducts: NMR (CDCl<sub>3</sub>) δ 1.57 (s, 6, isopropylidene), 3.56 (4-line m, 2, J<sub>α,pp</sub> = 1.6 Hz, α to carbonyl), 3.97 (t, 2, J = 1.7 Hz, bridgehead), 6.46 (t, 2, J = 1.7 Hz, vinyl).

**7-Isopropylidenebicyclo[2.2.1]heptane-2,3-cis-exo-dicarboxylic Anhydride.**<sup>21</sup> Exo adduct 14 (2 g) was dissolved in 100 mL of ethyl acetate and hydrogenated at atmospheric pressure, using 40 mg of 10% palladium on charcoal. The solution took up 1.2 equiv of hydrogen in 20 min, when the rate of uptake dropped sharply. The mixture was filtered through Celite and the solvent removed. Recrystallization from hexane–ethyl acetate gave crystals with mp 130–132 °C (lit.<sup>21</sup> mp 138 °C): NMR (CDCl<sub>3</sub>) δ 1.53 (d, 4, J = 2.8 Hz, methylene), 1.66 (s, 6, isopropylidene), 2.98 (s, 2, α to carbonyl), 3.20 (t, 2, J = 2 Hz, bridgehead).

**7-Isopropylidenebicyclo[2.2.1]heptane-2,3-cis-endo-dicarboxylic Anhydride.**<sup>21</sup> The mixture of endo and exo Diels–Alder adducts (3.3 g) was hydrogenated similarly with 60 mg of catalyst. The solution took up 1.5 equiv of hydrogen in 45 min. Workup similar to the above gave crude product containing 75% endo and 25% exo anhydride. Recrystallization from heptane or heptane–ethyl acetate gave mostly endo anhydride with mp 163–168 °C (lit.<sup>21</sup> mp 168–170 °C): NMR (CDCl<sub>3</sub>) 1.5–1.9 (bm, 4, methylene), 1.70 (s, 6, isopropylidene), 3.23 (bm, 2), 3.35 (bm, 2).

**7-Isopropylidenebicyclo[2.2.1]heptane-2,3-cis-exo-dicarboxylic Acid.**<sup>21</sup> The hydrogenated exo anhydride (12 g) was dissolved with warming in a small volume of Na<sub>2</sub>CO<sub>3</sub> solution. On acidification with dilute HCl, colorless crystals of the diacid precipitated, sometimes mixed with the anhydride: mp 181–183 °C (lit.<sup>21</sup> mp 184 °C dec); NMR (D<sub>2</sub>O) δ 1.39 (m, 4, methylene), 1.64 (s, 6, isopropylidene), 2.61 (s, 2, α to carbonyl), 2.80 (t, 2, J = 1.8 Hz, bridgehead).

**7-Isopropylidenebicyclo[2.2.1]heptane-2,3-cis-endo-dicarboxylic Acid.**<sup>21</sup> The hydrogenated endo anhydride (13 g) was treated in the same manner as the exo: mp 161–162 °C (lit.<sup>21</sup> mp 163 °C dec); NMR (CDCl<sub>3</sub>) 1.4–2.1 (bm, 4, methylene), 1.68 (s, 6, isopropylidene), 3.01 (bm, 2), 3.07 (bm, 2) 11.27 (bs, 2, carboxyl H).

**7-Isopropylidene-cis-exo-2,3-dicarbomethoxybicyclo[2.2.1]heptane, 16.**<sup>21</sup> The cis-exo anhydride (1 g) was refluxed in 16 mL of methanol for 1 h. The solvent was removed and replaced with ether. A solution of diazomethane in ether was then added until the solid had dissolved and the yellow color persisted. The ether was then evaporated on a

Table VII. NMR Spectral Data for 2,2-Dimethyl-3,4-dicarbomethoxybicyclo[3.3.0]oct-8-enes<sup>a</sup>

isomer	CH <sub>2</sub>	C-Me	BH	allylic CH <sub>2</sub>	α	α	CO <sub>2</sub> Me	vinyl
tF <sub>1</sub>	1.6-1.8 (bm)	1.00, 1.30	2.17 (m, <i>J</i> = 2.5?)	2.50, 2.60 2xq, overlapping, <i>J</i> = 2.5, 9.5)	2.73 (d, <i>J</i> = 10.5)	3.16 (d, <i>J</i> = 10.5)	3.69	5.28 (q, <i>J</i> = 2.5)
tF <sub>2</sub>	0.9-1.4 (bm)	0.95, 1.37	2.3 (m)	2.4-2.5 (bm)	3.03 (d, <i>J</i> = 10)	3.47 (d, <i>J</i> = 10)	3.66, 3.71	5.45 (q, <i>J</i> = 2.5)
cF <sub>1</sub>	0.95-1.5 (m)	1.11, 1.30	2.2-2.8 (m)	2.6 (m)	2.56 (d, <i>J</i> = 8.5)	3.25 (d, <i>J</i> = 8.5)	3.68	5.34 (q, <i>J</i> = 2.5)
cF <sub>2</sub>	1.4-1.8 (m)	1.28	2.03 (bm, d xdx?; <i>J</i> = 2.5, 5, 7.5)	2.49 (q?, <i>J</i> = 2.5), 2.5 (txd?, <i>J</i> = 5.5, 2.5)	3.08 (d, xd, <i>J</i> = 6.5, 2)	3.30 (d, <i>J</i> = 6.5)	3.62, 3.64	5.38 (q, <i>J</i> = 2.5)

<sup>a</sup> Coupling constants, *J*, in hertz.

steam bath and the solid recrystallized from ethyl acetate: mp 103-105 °C (lit.<sup>21</sup> mp 108 °C); NMR (CCl<sub>4</sub>) 1.1-1.6 (m, 4, methylene), 1.68 (s, 6, isopropylidene), 2.75 (s, 2, α to carbonyl), 2.94 (asymm t, 2, *J* = 2-2.5 Hz, bridgehead; collapses to s on irradiation at δ 1.3-1.4), 3.56 (s, 6, carbomethoxy).

**7-Isopropylidene-cis-endo-2,3-dicarbomethoxybicyclo[2.2.1]heptane, 18.**<sup>21</sup> The cis-endo anhydride (1 g) was treated in the same manner as the cis-exo anhydride; the product (18) had: mp 38-39 °C (lit.<sup>21</sup> mp 41 °C); NMR (CCl<sub>4</sub>) δ 1.1-1.5 (m, 4, methylene), 1.63 (s, 6, isopropylidene), 2.83 (bs, 4, α to carbonyl and bridgehead), 3.55 (s, 6, carbomethoxy).

**7-Isopropylidene-trans-2,3-dicarbomethoxybicyclo[2.2.1]heptane, 17.** The cis-exo diester 16 (1 g) was dissolved in a solution made by dissolving 30 mg of sodium in 15 mL of dry methanol and refluxed for 2 h. The cooled solution was acidified and extracted with ethyl acetate. The ethyl acetate solution was dried (MgSO<sub>4</sub>). The solvent was evaporated and the residue was slurried in ether and esterified with diazomethane. Low-temperature (-20 °C) recrystallization of the product from ethyl acetate gave crystals: mp 58-60 °C; NMR (CDCl<sub>3</sub>) δ 1.1-1.55 (m, 4, methylene), 1.59 (s, 3, isopropylidene), 1.65 (s, 3, isopropylidene), 2.8-3.0 (m, 3), 3.10 (q, 1, *J* = 4.5 Hz), 3.61 (s, 3, carbomethoxy), 3.67 (s, 3, carbomethoxy).

The trans diester 17 was also prepared by refluxing a solution of 1.0 g of dimethylfulvene and 1.4 g of dimethyl fumarate in 25 mL of benzene for 4 h. Removal of solvent, hydrogenation, and low-temperature recrystallization from ethyl acetate at -20 °C gave a modest yield of 17, mp 57.5-60 °C.

**Mass Spectra of Cycloadducts.** Mass spectra were taken of diesters 16-18, prepared by the Diels-Alder route, and of cycloadducts, using for the latter an inlet coupled to a Perkin-Elmer 990 gas chromatograph. All the spectra, including those of both bicyclo[2.2.1]heptanes and bicyclo[3.3.0]octenes, were very similar. The following are the 70-eV spectra for synthetic trans-bridged and for cF<sub>2</sub> adducts [given in the form, *m/e* (relative intensity of that ion in the spectra of tB and of cF<sub>2</sub>; tentative assignment)]: 254 (0.29, nd; M<sup>+</sup> + 2), 253 (1.7, 1.9; M<sup>+</sup> + 1), 252 (9.7, 10; M<sup>+</sup>), 221 (16, 19; M<sup>+</sup> - OMe), 220 (15, 10), 193 (10, 8; M - HCOOMe), 192 (63, 52; M - HCOOMe), 178 (9.8; M - COOMe, Me), 161 (10, 8; M - HCOOMe, OMe), 145 (38, 61; protonated dimethyl fumarate), 134 (11, 11), 133 (100, 100; M - HCOOMe, COOMe), 132 (44, 10), 117 (11, 17), 114 (16, 12), 113 (66, 53), 108 (10, 13), 107 (42, 39), 106 (28, 15), 105 (25, 19), 93 (38, 29), 91 (48, 35), 79 (22, 14), 77 (16, 15), 59 (11, 7), 41 (19, 37), 39 (10, 1.3).

**Effect of Lanthanide Shift Reagent on NMR Spectrum of cF<sub>2</sub> 21 or 22.** The cis-fused diester (89 mg) of longer retention time (cF<sub>2</sub>), separated by preparative GC, was dissolved in carbon tetrachloride, and successive mole ratios of 0.1, 0.2, 0.4, and 0.6 of Euroshift reagent (Pierce Chemical Co.) [Eu(F<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>CCOCHCO<sub>*t*</sub>-Bu)<sub>3</sub>] were added. The shift reagent removed the accidental degeneracy of the two methyls and of the two carbomethoxy groups. At 0.4 mol ratio the *gem*-dimethyl groups were shifted to δ 1.8 and 2.5, and the carbomethoxys to δ 4.9 and 5.5. Above 0.2 mol ratio the spectrum broadened so that no fine structure could be observed.

**Epimerization of Fused Esters 21-24.** Solutions of each of the four fused esters (100 μL, about 0.1-0.2 M in CH<sub>3</sub>OH) were mixed with an arbitrary amount of diphenyl ether as internal standard and analyzed by GC for relative amounts of ester and standard. They were then mixed in 7-mm Pyrex sample tubes with an equal volume of fresh 0.1 M sodium methoxide solution prepared by dissolving 23 mg of sodium in 10 mL of methanol. The tubes were sealed and heated at 90 °C for 15 h or 130 °C for 4 h. After the 90 °C heating there was

partial conversion of cF<sub>2</sub> to tF<sub>1</sub> and of cF<sub>1</sub> to a 5:1 mixture of tF<sub>1</sub> and tF<sub>2</sub>. The trans-fused esters were not affected. After the 130 °C heating all the cis-fused esters had been epimerized to trans-fused, but the trans-fused had not reached equilibrium. Recovery of epimerized esters was 50-85% of starting ester, based on internal standard.

Control experiments showed that dimethyl fumarate initially containing <0.001% dimethyl maleate and dimethyl maleate initially containing 0.7% dimethyl fumarate could be recovered unchanged after having been heated at 58 °C for 12 h with diazene 1 in methyl acetate. Also, decomposition of diazene 1 in acetonitrile solution containing a mixture of dimethyl maleate cycloadducts caused no change in the cycloadduct composition.

**Detector Response and Use of Internal Standard.** In order to determine the yield of adducts and dimers, a weighed amount of compound inert to the reaction conditions and easily separated by GC was added to the reaction mixture. The relative response of the flame ionization detector to the three types of compounds was determined; it was assumed that isomers would have the same response.

Crystalline biradical dimer (one isomer by GC on Carbowax 20 M) was obtained by pyrolysis of azo compound in an inert solvent. Diphenyl ether, an inert compound of suitable retention time, was purified by preparative GC on column E at 160 °C. For a cycloadduct isomer, trans-bridged diester 17 was available in crystalline form by synthesis. A mixture of about 10 mg of each compound was carefully weighed and then dissolved in chloroform. Each sample was analyzed at least three times, integrating the peak areas with the electronic integrator. The relative response (per unit weight) of two compounds 1 and 2 was determined from the expression  $RR = A_1W_2/A_2W_1$ , where *A* is peak area and *W* is weight. A series of analyses on a 5-ft × 1/8 in. o.d. 5% FFAP column at 160 °C gave values of responses of dimer relative to diphenyl ether of 1.052 ± 0.006 and of diester to ether of 0.629 ± 0.016 (the error estimate is the standard deviation of the mean). A later series on a 5-ft × 1/8 in. 5% XE-60 column with a temperature program gave values of 1.03 and 0.600. Averages of these two sets of values were used in all subsequent calculations.

**Concentration of Samples.** In analyzing pyrolyses run at high dilutions, it was necessary to concentrate the sample in order to get a satisfactory GC response. This was done by directing a stream of nitrogen into the sample tube through a large syringe needle, stopping the nitrogen flow before all solvent evaporated. The extent of differential evaporation of dimers, standard, and cycloadducts was checked. For example, addition of 2 mL of acetonitrile to a sample tube containing approximately 2 mg of dimer, standard and cycloadducts (the lowest concentration studied) and evaporation to a final volume of about 20 μL caused a 1% increase in the ratio of adducts to standard and a 4% decrease in the ratio of dimers to standard. The variation in the relative yield of different cycloadducts was 1% at worst, generally better, or about the same as the reproducibility (ca. 0.3%) of two successive analyses of the same solution.

The concentrations given in Table IX for the dimethyl fumarate runs are corrected for vaporization of the solvent. The correction is largest for the more concentrated samples, where the amount of vapor in equilibrium with the liquid phase constitutes a larger fraction of the total. Dimethyl maleate concentrations (Table VIII) are nominal and are not corrected for solvent vaporization.

**Pyrolysis of Diazene 1 with Dimethyl Maleate.** A stock solution of 10:1 mol ratio of dimethyl maleate to azo compound plus internal standard was diluted with acetonitrile. The quantity of stock solution used at each dilution was varied so that a similar absolute yield of adducts was produced; i.e., since the product composition tended toward more dimer and less adduct at high dilution, the amount of

**Table VIII.** Composition of Product Mixtures from Pyrolysis of Diazene **1** in the Presence of Dimethyl Maleate in CH<sub>3</sub>CN at 60 °C

[DMM], M	% product					total adducts
	tF <sub>1</sub>	tB	tF <sub>2</sub> + cF <sub>1</sub>	cF <sub>2</sub>	cB	
6.6	9.9	22.7	30.0	34.7	2.9	95
3.3	11.3	25.1	29.8	32.0	1.8	95
1.32	16.9	36.7	22.3	20.2	4.0	93
0.66	18.8	43.6	19.4	14.1	4.2	86
0.33	21.5	49.1	15.7	7.9	6.0	59
0.13	22.4	51.1	14.6	6.3	5.5	38
0.066	23.2	52.0	14.1	5.5	5.4	24
0.033	24.4	51.2	12.9	5.4	6.1	12

**Table IX.** Composition of Product Mixtures from Pyrolysis of Diazene **1** in the Presence of Dimethyl Fumarate in CH<sub>3</sub>CN at 60 °C

[DMF], M	% product					total adducts
	tF <sub>1</sub>	tF <sub>2</sub>	tB	cF <sub>2</sub>	cB	
0.515	51.4	38.1	9.9	<sup>a</sup>	0.6	100
0.204	48.7	32.5	17.6	<sup>a</sup>	1.2	100
0.0725	42.8	23.0	30.3	<sup>a</sup>	3.9	<sup>a</sup>
0.035	39.2	18.0	36.9	0.05	5.9	<sup>a</sup>
0.017	37.9	14.0	41.2	0.4	6.5	98.5
0.007	36.8	11.6	44.5	0.12	7.0	95.6

<sup>a</sup> Not determined.**Table X.** Composition of Solutions for Kinetics

solution	[I], M	[fumarionitrile], M		solvent, μL	
		A, μL	B, μL	A, μL	B, μL
1	0.194	0	0.0	100	400
2	0.194	0.10	62.5	100	337.5
3	0.194	0.20	125	100	275
4	0.194	0.40	250	100	150

**Table XI.** Kinetics of Thermal Decomposition of **1** at 52 °C in *o*-Dichlorobenzene (Solution No. 2)

time, s	peak ht <sup>a</sup>		$k \times 10^4$ , s	
	$\delta$ 5.37	$\delta$ 1.63	$\delta$ 5.37	$\delta$ 1.63
0	4.3	22.8	2.00	1.25
1800	3.0	18.2	1.33	1.52
5400	2.1	10.0	1.42	1.31
9000	1.2	7.0	1.33	1.40
12600	0.8	3.9		

av: 1.5 ± 0.16

<sup>a</sup> Relative to internal standard = 1.35.

stock solution was increased in proportion. The highest concentration employed was the neat stock (no solvent) and the lowest a 200:1 dilution of this. The samples were diluted and the tubes sealed as described previously, and the sample tubes were heated overnight at 60 °C or photolyzed for 2 h in the Rayonet reactor. Independent UV analysis of samples 2.0 and 0.2 M in dimethyl maleate after several irradiation times established that 2 h was more than sufficient to decompose all azo compound. The samples were analyzed on column A at 150 °C. The results are given in Table VIII. Because the analyses of relative amounts of adducts formed were much more reproducible than those of the amounts of adducts and dimers relative to internal standard, the tables give relative yields of adducts and absolute yields of total adducts, the rest of the products being dimers.

**Pyrolysis of Diazene 1 with Dimethyl Fumarate.** Stock solution of 10:1 (mol ratio) dimethyl fumarate and azo compound plus internal standard was made up to 0.34 M in dimethyl fumarate with CH<sub>3</sub>CN. The samples were treated like the maleate ones; the analysis results

are presented in Table IX. The yields of adducts were taken from smoothed curves; the remainder of the products consisted of dimers.

**Kinetics of the Thermal Decomposition of Diazene 1 in the Presence of Fumarionitrile.** A solution of fumarionitrile (626.2 mg) made up to 10.0 mL with *o*-dichlorobenzene was prepared and labeled A. A solution of diazene **1** (131.6 mg) made up to 1.00 mL with *o*-dichlorobenzene was labeled B. From these two solutions, the solutions in Table X were prepared. These four solutions were placed in NMR tubes, and analyzed by NMR at various times (0, 30, 90, 150, and 210 min), while being heated at 52 °C.

The decomposition was monitored by NMR using the solvent peaks as internal standard and following the bridgehead ( $\delta$  5.37) and isopropylidene ( $\delta$  1.63, superimposed on a broad resonance between  $\delta$  1.0 and 1.9) resonances of **1**. A typical run is given in Table XI. Solutions 1–4 gave values for  $k \times 10^4$ , s, of 1.7, 1.5, 1.6, and 1.5.

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## References and Notes

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