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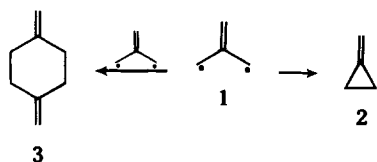
Direct Measurements of the Absolute Rates of Dimerization and Capture of the 2-Isopropylidenecyclopenta-1,3-diyl Species by Electron Paramagnetic Resonance Spectroscopy

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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 vapor[3] and from the benzene-sensitized photolysis of 4-methylenepyrazoline[4] 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**.[6] 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.
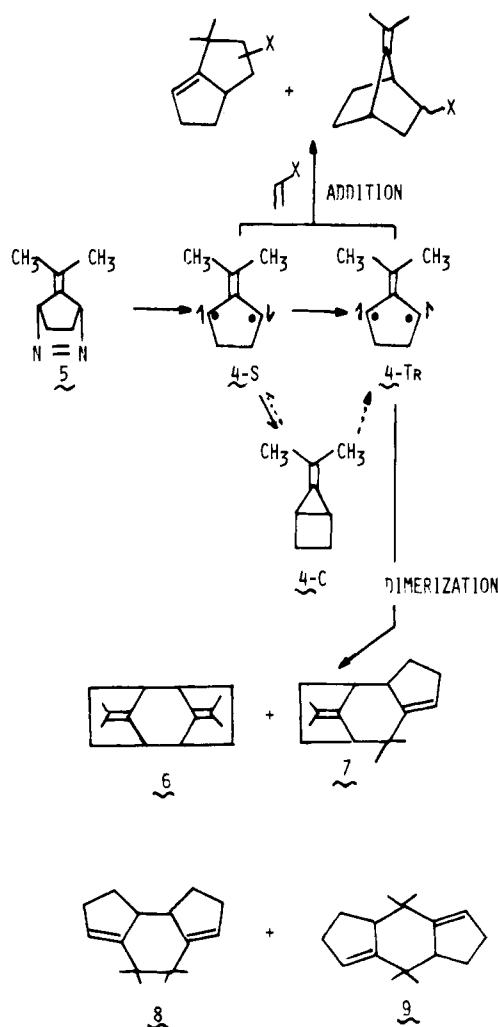
Conditions for Kinetic Measurements on Triplet Molecules in Fluid Media by EPR Spectroscopy. The basic EPR technique we use is an adaptation of the one worked out by Ingold and his associates.[10] The concentration of paramagnetic species is determined after calibration of the EPR spectrometer response using a known concentration of a stable free radical, typically diphenylpicrylhydrazyl (DPPH) or di-*tert*-butylnitroxyl (DTBNO). In the calibration, the first derivative spectrum of a known concentration of standard radical is recorded, and then the trace is digitized and double integrated to obtain the signal area. The spectrometer response factor, C, is defined in eq 1, where the signal is adjusted to unit receiver gain.

$$[\text{radical}] = C(\text{signal area}) \qquad (1)$$

The transient radical concentration is determined using the same volume of solution and the same EPR sample tube as the standard. Digitization and double integration, as before, give the signal area and, via eq 1, the concentration.

At the time of this work,[1] we were unable to find any reports of the use of EPR kinetics to determine the rates of reaction of triplet molecules in solution.[11] Undoubtedly, the kinetic instability of many triplet molecules and the unsatisfactory EPR spectra of rapidly tumbling triplets have contributed to the absence of research activity in the field.

In fluid media, there are two major mechanisms by which the quality of a triplet EPR spectrum can be degraded. Spin-lattice relaxation tends to produce broad, difficultly observable lines, whereas rotational averaging of the direct magnetic dipolar coupling between the two electrons can collapse the (normally six) $\Delta M_s = 1$ transitions observed in rigid, randomly oriented samples to a single line. In the latter case, the triplet signal would become difficult to distinguish from doublet impurity peaks.

Weissman[12] has calculated that, for most organic molecules, τ_c, the rotational correlation time, must be in the range of $10^{-11}-10^{-12}$ s in order to cause uncertainty narrowing of a 2000-G dipolar splitting to 20 G. Experimentally, he demonstrated that there was no narrowing of the dipolar splitting of the dimeric association complex [Na$^+$ fluorenone$^-$]$_2$ when τ_c $\sim 10^{-4}$ s. Even when $\tau_c \sim 10^{-7}$ s, narrowing and distortion of the triplet signal were barely discernible. For our triplet molecule **4**, which has a total $\Delta m_s = 1$ spectral width of about 600 G, the τ_c values needed to preserve signal quality would be increased but only by about a factor of 3–4.

From the Einstein relation, $\tau_c = 4\pi\eta a^3/3kT$, and the approximate molecular radius of **4**, $a \sim 2.5$ Å, we may calculate that $\tau_c \gtrsim 10^{-7}$ s will be achieved at 150 K in solvents of moderate viscosity, $\eta \sim 30$ P (compare water, $\eta \sim 0.01$ P, and glycerol, $\eta \sim 15$ P, at room temperature).

Our kinetic experiments employ as solvent a mixture of 2 parts of 1-propanol to 3 parts of 2-propanol, $\eta = 2000$ P,[13] at our reaction temperature of 143.6 K. This provides a safety factor of almost two orders of magnitude relative to the 10^{-7} s distortion limit of τ_c and about five to six orders of magnitude relative to the "collapse" limit of $10^{-11}-10^{-12}$ s. That the medium also is chemically unreactive to diyl **4** is established not only by previous experience[6,14] but also by the kinetic behavior to be described.

Experimental Section

The EPR spectrometer is a Varian E-9 unit equipped with a variable temperature accessory. Temperature control to within ±0.1°C for 40 min over the range -190 to $+100$ °C is achieved with the manufacturer's standard arrangement, which consists of a vacuum-jacketed, silvered quartz tube to direct a flow of cold nitrogen over the sample in the spectrometer cavity, a platinum sensor, and a filament heater, both connected to a remote proportional control unit. A Pyrex tube containing the probe of an iron–constantan thermocouple is placed

on top of the sample tube and serves to stabilize it in the nitrogen stream. The temperature is determined by measurement of the thermocouple voltage with a Leeds and Northrup millivolt potentiometer. Any error introduced by temperature differences between the sample and the thermocouple well is considered to be small relative to the other errors of the kinetic measurements. Irradiation of the sample in the spectrometer cavity is achieved with a 200-W Oriel Short Arc mercury lamp equipped with a collimating lens.

Qualitative Behavior of 5 upon Photolysis. Continuous irradiation of a degassed 1–2 M solution of the diazene **5** in the mixed propanol solvent at -129.5 °C (143.6 K) through a CuSO$_4$ filter (to remove infrared light and reduce heating of the sample) produces an EPR signal that quickly rises to a steady-state level and remains as long (typically several hours) as the concentration of **5** is sufficiently high. Continued irradiation beyond that point results in a decline of the signal. Similarly, a steady-state signal cannot be achieved starting with low concentrations (<0.02 M) of **5**. Under rigid matrix conditions, irradiation causes the signal to rise, pass through a maximum, and slowly decline. This behavior seems to be due to the photolability of the diyl **4**.[15] At low enough diazene concentration, diyl **4** can act as an internal filter and suffer photodecomposition.

The yield of TMM dimers from the complete photolysis of 0.0144 M diazene **5** in propanols at 143.6 K is 74 $\pm$ 3% (average of three determinations) by gas chromatographic (GC) analysis with tetradecane as an internal standard ($\frac{1}{8}$ in. $\times$ 5 ft, SE-30, 1% Chromosorb Q column). Presumably, the missing 26% of material is accounted for as rapidly eluted (monomeric) photolysis products of the diyl **4**[16] which emerge with the solvent peak in GC.

Further information on the photolability of triplet diyl **4** comes from GC analysis ($\frac{1}{8}$ in. $\times$ 5 ft UCONLB55OX on 100/120 Chromosorb P) of the products of photolysis (2537 or 3500 Å) of solutions of **5** in 1:1 methylcyclohexane–methylcyclopentane glass at 77 K. The chromatograms show, in addition to dimers, a set of six peaks with shorter retention times, four of which are approximately the same as those of the hydrocarbons **10–12** previously characterized as products

10 **11** **12a,** R$_1$ = H; R$_2$ = Me
            b, R$_1$ = Me; R$_2$ = H
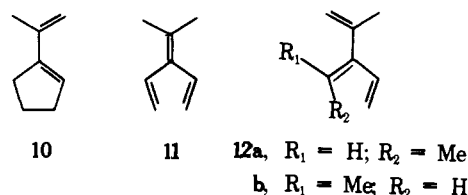
of the gas-phase flash-vacuum pyrolysis of **5**.[17] Only one peak is produced when the irradiation beam is passed through a Pyrex filter (3100-Å cutoff).

Constant illumination of a glassy sample in diethyl ether at 77 K causes a rapid rise of the EPR signal to a maximum value, where the signal briefly levels off and then declines in an almost linear manner (plot of the peak height of the strongest EPR transition vs. time). If the irradiation is stopped at any point along the decay curve, the EPR signal is indefinitely stable. Resumption of the illumination again causes the signal intensity to decline. Clearly the triplet-destroying process under these rigid glass conditions is a photochemical reaction.

The yield of the volatile product (retention time the same as that of **10**) increases with increasing duration of illumination, as determined by GC analysis of the molten reaction mixtures, using adamantane as an internal standard. A graph of this behavior is given as Figure 1.

Preparation of Samples. A solution of 20–100 mg of diazene **5**,[6] recrystallized from pentane, in 100–200 μL of solvent (2 volumes of 1-propanol, 3 volumes of 2-propanol) which had been distilled and stored over molecular sieves is transferred by syringe into a 1-in. section of 4-mm quartz tube sealed at the bottom and joined by a graded seal to Pyrex at the top. The open Pyrex section is attached to a vacuum (0.1–0.5 Torr), subjected to three freeze–pump–thaw cycles, and sealed in the Pyrex region. During the thaw cycle, the matrix is warmed slowly from the top to prevent rapid expansion of the sample, which might have shattered the cell.

Kinetics of Dimerization. When the initial concentration of diazene **5** is 1–2 M, a steady-state EPR signal of triplet **4** is achieved within seconds after the initiation of steady illumination of the sample at 143.6 K. Under these conditions, the triplet spectrum is not distorted, but an accurate integration cannot be obtained directly. The signal-
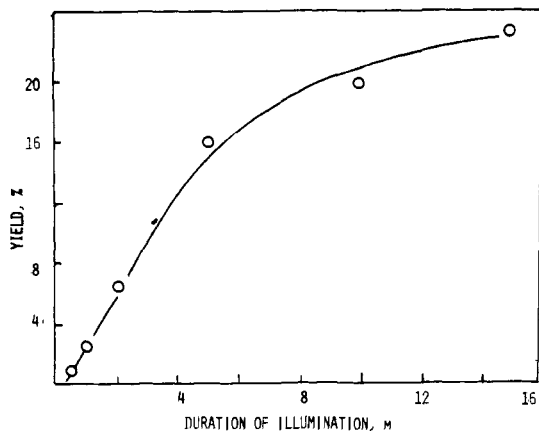
Figure 1. Yield of product with the GC retention time of **10** in the photolysis of **5** in 1:1 methylcyclohexane–methylcyclopentane glass at 77 K.
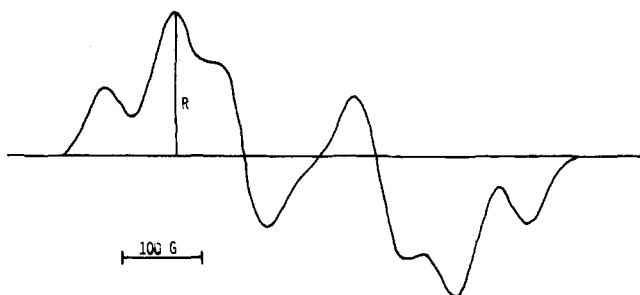

Figure 2. Determination of the EPR signal peak height at maximum amplitude in the $\Delta m_s = \pm 1$ spectrum of **4** in a rigid propylene glycol glass at 143.6 K.

to-noise ratio is low because the triplet concentration is low (steady-state condition). Moreover, there is a large extraneous peak in the center of the spectrum due to a doublet impurity. We use an empirical calibration to circumvent this difficulty and provide a measure of the integrated EPR absorption area, which in turn is proportional to the triplet concentration.

A solution of **5** in propylene glycol at 143.6 K corresponds to a static EPR system, since the medium is highly viscous. Irradiation gives a doublet-free spectrum with high signal-to-noise ratio which can be integrated accurately, and from this we obtain the values (two runs) $R = 4.14$ and 4.47×10^4 G/chart unit for the ratio of the integrated area to peak height at the magnetic field of maximum absorption (see Figure 2). On the assumption that the ratio R is the same in the propanol mixture used for the kinetic measurements, we follow the concentration of triplet **4** by measuring the change in peak height at the same magnetic field. The assumption is valid because the EPR spectra under kinetic and static conditions have the same line shape, even though they differ in signal-to-noise ratio. This is because, even under kinetic conditions, molecular reorientations are slow enough so that the signal is not distorted. Note that R is independent of the receiver gain.

Integration of the EPR derivative trace is achieved by breaking it into many points connected by straight lines followed by double integration using a computer program written by Professor J. M. McBride for the Wang 2200 calculator. If high peak-to-peak modulation is used, less than 100 points are needed to give a good approximation of the derivative trace.

In the kinetic runs, we measure the peak height of the absorption maximum of **4** at the steady-state concentration, using a convenient receiver gain and the 0.2-mW setting of microwave power to avoid saturation of the signal. The observed value is linear in receiver gain (rg) and is normalized to unit rg by dividing the peak height by the experimental rg. Using the R value obtained from the spectrum in propylene glycol and the spin-count calibration to be described, we can convert the observed peak height to an absolute concentration of **4**. The microwave power now is raised from 0.2 to 10–30 mW. During this amplification, the triplet concentration remains unchanged (steady-state conditions), but the signal-to-noise ratio is greatly im-
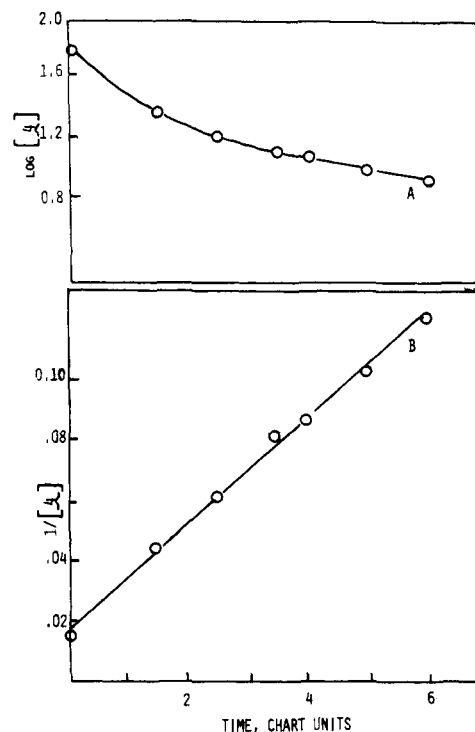

Figure 3. Function of concentration vs. time for the decay of the EPR signal of **4** in propanol at 143.6 K plotted as (A) first order, (B) second order. The last point represents about 3 reaction half-lives.

proved because many more transitions among the triplet sublevels are stimulated. The new signal, adjusted if necessary with rg, is briefly recorded to establish the deflection corresponding to the new instrument settings and the known concentration of **4**, then the light shutter is closed, marking time zero, and the decline of the signal is recorded. At the higher power levels, there is some concern that differential saturation may cause weakening of the signal at the later kinetic points, but this does not seem to be a problem, at least during the 2–3 half-lives of reaction we usually followed. Also, observations elsewhere[7] showed that saturation was not observed above 14 K. Figure 3A shows a typical kinetic run at 143.6 K plotted as a first-order reaction and Figure 3B shows the same data plotted in second-order fashion. The reaction is examined for 3 half-lives and behaves as a second-order process.

Spin-Count Calibration of Absolute Concentrations of Triplet 4. To estimate the absolute accuracy of the spin-count method, we compare the gravimetric concentration of a sample of DTBNO to that calculated from its signal strength relative to a DPPH standard. A 5.63×10^{-4} M solution of DPPH in mixed propanol solvent made up at 22 °C shows a signal intensity at 22 °C of 71.4 G^2 normalized to unit rg. From this and eq 1, we calculate the instrument response factor under these conditions as $C = 7.90 \times 10^{-6}$ M/G^2. At the same temperature, a 9.35×10^{-3} M solution of DTBNO gives a normalized signal area of 1.54×10^{-3} G^2. From eq 1 and the above value of C, we calculate [DTBNO] as 12.2×10^{-3} M, which corresponds to an error of +28%. In a second experiment with these samples at 143.6 K assuming a 20% volume contraction,[18] [DPPH] = 7.04×10^{-4} M and [DTBNO] = 11.2×10^{-4} M. We find $C = 1.58 \times 10^{-6}$ M/G^2 and a normalized signal area of 4.45×10^2 G^2 for DPPH. The normalized signal for DTBNO is 4.29×10^3 G^2, from which we calculate [DTBNO] = 6.8×10^{-3} M, which corresponds to an error of -39%.

In comparing the signal intensity of our triplet **4** with that of the doublet calibration standards DPPH or DTBNO, we must take into account a statistical correction[19] which makes the signal associated with an EPR transition in the triplet inherently 1.33 times as intense (per electron) as that in a doublet. Because the g factors of the reference free radical and the triplet are nearly the same, ΔN, the Boltzmann population difference between adjacent spin states of the doublet and triplet, will be essentially the same. At 143.6 K, ΔN will be small, and the unpaired electrons in two doublets will be almost equally divided among four spin states, whereas those in the triplet will be distributed over three spin states. For the two doublets, we have $N_\beta = (\frac{1}{4})(N + \Delta N)$ and $N_\alpha = (\frac{1}{4})(N - \Delta N)$; for the triplet, we have

Table I. Absolute Rate Constants (k_2) for Dimerization of **4** in Propanols at 143.6 K

run	steady state peak ht (0.2 mW)	(integral)$_{rg=1}$ [c]	[triplet]$_0$[d] $\times 10^5$ M^{-1}	steady state peak ht (high power)	k_2[e] $\times 10^3$ M s
1[a]	15.0	125	7.38	63	3.13
2[a]	15.5	129	7.64	72	2.37
3[a]	26	135	8.00	90	1.73
4[a]	12	99.4	5.87	66	3.52
5[a]	24	124	7.33	66	2.59
6[b]	30	284	8.97	60	2.42
7[b]	57	270	8.53	69	2.04
8[b]	61	289	9.12	81	1.16
9[b]	21	195	6.16	63	1.47
10[b]	23	218	6.88	86	1.12
					av ± 2 s = $\overline{2.2} \pm 1.3$

[a] Data set 1. $C_{DPPH} = 1.58 \times 10^{-6}$ M/G^2. Propylene glycol triplet standard $R = 4.14 \times 10^4$ G/chart unit. $C_{triplet} = (^3/_8)C_{DPPH} = 5.92 \times 10^{-7}$ M/G^2. [b] Data set 2. $C_{DPPH} = 8.50 \times 10^{-7}$ M/G^2. Propylene glycol triplet standard $R = 4.47 \times 10^4$ G/chart unit. $C_{triplet} = (^3/_8)C_{DPPH} = 3.16 \times 10^{-7}$ M/G^2. [c] By double integration of the digitized trace and division of the integral by the receiver gain. [d] Steady-state triplet concentration = (peak height in chart units at 0.2 mW)(R in G^2/chart unit) ($C_{triplet}$ in M/G^2). [e] Determined graphically from the slope of the plot of 1/[triplet] vs. time in seconds.

Table II. Kinetics of Cycloaddition of the Triplet TMM **4** to Olefins in Mixed Propanols at 143.6 K[a]

olefin	[olefin]	k'_a, s^{-1}	k_a, M^{-1} s^{-1}	k_a, M^{-1} s^{-1} (av)
dimethyl fumarate	0.12	0.43, 0.39, 0.41, 0.37, 0.33	3.59, 3.25, 3.41, 3.09, 2.75	3.2
fumaronitrile	0.30	0.33, 0.29, 0.325, 0.302, 0.276	1.1, 1.0, 1.1, 1.0, 0.92	1.0
acrylonitrile	1.78	0.338, 0.392, 0.405, 0.434, 0.397	0.19, 0.22, 0.23, 0.24, 0.22	0.215
acrylonitrile	1.78	0.368, 0.321, 0.330, 0.322	0.21, 0.18, 0.19, 0.18	0.195
acrylonitrile	1.42	0.294, 0.294, 0.273, 0.294	0.21, 0.21, 0.19, 0.21	0.20
acrylonitrile	1.07	0.201, 0.203, 0.215, 0.218, 0.213	0.19, 0.19, 0.20, 0.20, 0.20	0.20
styrene	1.20	0.120, 0.137, 0.134, 0.157	0.10, 0.11, 0.11, 0.13	0.115
1,3-cyclohexadiene	1.67	0.256, 0.287, 0.293, 0.230	0.15, 0.17, 0.18, 0.14	0.16

[a] Rate constants determined graphically or by least-squares analysis of plots of log [relative EPR signal intensity] vs. time. The rate constants are defined in eq 2.

$N_- = (^1/_3)(N + \Delta N)$, $N_0 = (^1/_3)(N)$, and $N_+ = (^1/_3)(N - \Delta N)$. The transition probability per electron is proportional to the population difference of the spin levels concerned. The ratio of triplet and doublet transition probabilities is then $(^1/_3)/(^1/_4) = ^4/_3$ per electron, or $^8/_3$ for two electrons. The total $\Delta m_s = \pm 1$ envelope of the triplet therefore should be $^8/_3$ as intense as the band produced by an equal concentration of the doublet reference. The instrument response factor (C, eq 1) then is defined as $C_{triplet} = (^3/_8)C_{doublet}$.

The data and calculations for two complete procedures involving five kinetic runs each appear in Table I. The imprecision of the spin count is reflected in the spread of rate constants observed, but there is overlap between the two data sets. Base-line drift contributes a small imprecision to the data. With second-order kinetics, it makes data points beyond 3 half-lives very unreliable. In this work, kinetic runs where the base line remains constant to within one or two spectrometer chart units give good second-order plots (see Figure 3). When the base-line drift is severe, the run is discarded. For each kinetic run, the reaction order, n, also is crudely checked with the aid of the equation[20] $\log (t_{1/2}) = \log D - (n - 1) \log [4]_0$, where D is a constant. In all instances, $2.2 \leqslant n \geqslant 1.7$.

Kinetics of Cycloaddition. These measurements use many of the same experimental techniques as the dimerization study. However, the concentrations of reactants are adjusted to ensure pseudo-first-order conditions. As we have seen, photolysis of 0.01–0.1 M diazene **5** gives steady-state concentrations 10^{-5}–10^{-4} M in triplet **4**. The concentration of olefin [Y] is typically 0.1–1.0 M, so that the olefin is in large excess throughout the reaction. Under these conditions the rate law becomes

$$d[triplet]/dt = k_a[triplet][Y] = k_a'[triplet] \qquad (2)$$

The measurements are inherently far more accurate than the dimerization measurements, because we need not know the absolute triplet concentration.

One minor difficulty arises if the light intensity and the diazene concentration are both high. These conspire to produce a high steady-state concentration of triplets, so that dimerization becomes competitive with cycloaddition. (The rate constant for dimerization is several thousand times that for cycloaddition, which balances the concentration ratio of triplet to olefin.) To circumvent this problem, one either may reduce the light intensity with a neutral density filter or ignore the kinetic data of the first half-life of the reaction. Both methods give identical rate constants.

The cycloaddition kinetics are strictly pseudo first order. A typical curve of the decay of the EPR signal plotted in first-order form is shown in Figure 4, and the kinetic data are summarized in Table II. In the case of acrylonitrile, the reaction is shown to be first order in olefin by variation of the olefin concentration, which produces a linear response in the pseudo-first-order rate constant (Table II).

The major errors in the rate constants probably arise from the temperature variation (probably ± 0.5 °C) and from the assumption that the solvent contraction of about 20% measured in other cases[18] applies here. A conservative estimate of the overall uncertainty in the rate constants might be 10%, although the reproducibility is much better (2 standard deviations, ~5%).

The olefins listed in Table II are obtained commercially and purified by distillation or crystallization. EPR samples are degassed and sealed as for the dimerization kinetic runs. Independent control experiments provide the material balance of dimers and cycloadducts obtained by exhaustive photolysis of diazene **5** in the presence of olefin in mixed propanols at 143.6 K with diphenyl ether internal standard. GC response factors and product analyses are determined with a 10 ft $\times$ $^1/_8$ in. 10% DCSSO on 80/100 Chromosorb P column. This column separates adducts from dimers in each case but is not useful for the analysis of individual adducts. The material balance data are shown in Table III. We assume (as before) that the shortfalls from quantitative yields are the result of secondary photolysis. The formation of substantial amounts of dimers despite the clean pseudo-first-order kinetics is not unexpected, since, as already has been stated, the kinetic runs use only later data points or filtered light. Another possible source of both dimers and adducts may be some 5-isopropylidenebicyclopentane, which is the major product of photolysis of **5** at somewhat higher temperatures, is thermally stable at 143.6 K,[6c] but would react at the much higher temperatures of the GC analysis. These product-forming pathways have no effect on the EPR kinetics.
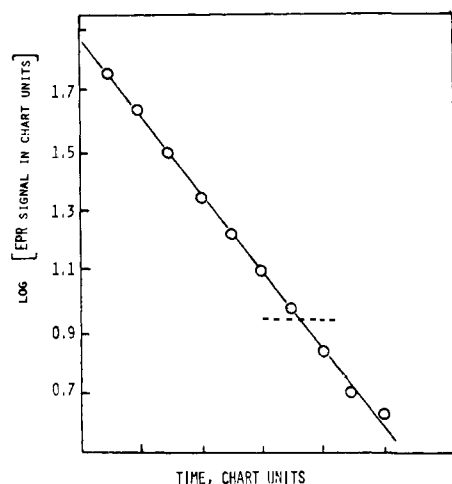
Figure 4. First-order plot of EPR signal intensity in the reaction of triplet diyl **4** with acrylonitrile in mixed propanols at 143.6 K. The dashed line represents 3 half-lives of reaction.

The Arrhenius parameters for the reaction of triplet **4** with acrylonitrile are determined at seven temperatures over the range 120.8–143.6 K. At least three determinations are made at each temperature, and good pseudo-first-order behavior is observed in all instances. The data are presented in Table IV. The values $E_a = 6.0$ kcal/mol and log $A = 8.7$ (A in M^{-1} s^{-1}) are obtained by least-squares analysis ($r = 0.994$) of the plot of ln k_a vs. $1/T$.

Results and Discussion

Dimerization. The second-order dimerization rate constant, $k_2 = (2.2 \pm 1.3) \times 10^3$ M^{-1} s^{-1} (Table I), although not highly accurate, permits certain mechanistic conclusions about the reaction by a comparison with the encounter-controlled rate. Using the Debye–Stokes–Einstein diffusive model,[21] we may calculate the bimolecular diffusion-controlled rate constant from eq 3 and the viscosity of the mixed propanolic medium ($\eta = 2000$ g cm^{-1} s^{-1}) as $k_d \sim 1.6 \times 10^4$ M^{-1} s^{-1} at 143.6 K.

$$k_d = 8RT/3000\eta \qquad (3)$$

Dimerization thus is about 0.13 times (about $\frac{1}{9}$) the encounter frequency. Theoretically, a statistical factor of $\frac{1}{9}$ would be applicable to a triplet + triplet dimerization if both new carbon–carbon bonds were formed simultaneously, since the interaction of two triplets can give rise to nine spin states in the encounter complex (five quintets, three triplets, and a singlet), only one of which is suitable for a spin-allowed conversion to singlet product. However, we refrain from urging this "spin-sorting" interpretation of the apparent agreement between the statistical ratio and k_2/k_d, because the k_2 value is uncertain to about 50-60%, and, moreover, there is evidence in the literature[21-23] that k_d values, especially in hydroxylic solvents, may be as much as twice the k_d calculated from the Debye–Stokes–Einstein model.

Nevertheless, the k_2 value may be used in another way to construct an argument that dimer formation is a triplet + triplet (Tr + Tr) reaction. The observed second-order rate law is a necessary but insufficient condition for this mechanism. A singlet + triplet (S + Tr) reaction also would produce this kinetic behavior if S were generated from Tr by a rapid equilibrium Tr $\rightleftharpoons$ S, with equilibrium constant K. The observed rate constant, k_2, then would be related by eq 5 to the S + Tr mechanistic reaction rate constant k of eq 4. However, it may be shown that k, the rate constant for the alleged S + Tr reaction, would have to be improbably large to fit the data.

$$-d[Tr]/dt = kK[Tr]^2 \qquad (4)$$

$$k_2 = kK \qquad (5)$$

Table III. Material Balance of Dimers and Cycloadducts from Photolysis of Diazene **5** and Olefins in Mixed Propanols at 143.6 K

[5], M	[olefin], M	yield, %[a]		
		adduct	dimer	total
0.0361	CH₂=CHCH, 3.39	51	31	82
0.0289	CH₂=CHCN, 2.71	62	22	84
0.0217	CH₂=CHCN, 2.03	83	10	93
0.0265	PhCH=CH₂, 1.01	27	63	90
0.102	1,3-cyclohexadiene, 2.29	11	76	87
0.0294	fumaronitrile, 0.53	98 ± 18	14	112 ± 18
0.0359	dimethyl fumarate, 0.073	26 ± 7	74 ± 3	73 ± 10

[a] Absolute, based on Ph₂O internal standard. The experimental error on the first five runs is <3% absolute.

Table IV. Temperature Dependence of the Rate of Reaction of Triplet **4** with Acrylonitrile in Mixed Propanols

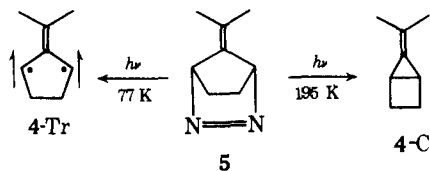| temp, K	k_a, M^{-1} s^{-1} [a]	temp, K	k_a, M^{-1} s^{-1} [a]
120.8	0.0359	136.1	0.0823
123.8	0.0638	139.6	0.174
127.0	0.0175[b]	143.6	0.215
132.5	0.0427		

[a] The rate constants are obtained by division of the observed pseudo-first-order rate constant by 1.46 M, the concentration of acrylonitrile. [b] Average of four determinations. Other values are averages of three determinations each.

We may estimate an upper limit for K by consideration of the energy separation between the triplet and lowest singlet states of diyl **4**. In crystalline diazene **5** as host, the EPR signal intensity of the triplet ground state of **4** obeys the Curie law over the temperature range 14–268 K,[7] which means that the energy of S lies at least 600 cal/mol above that of Tr. This estimate may well be extremely conservative, since an experimental determination by another technique[24] permits a separation of up to 3.5 kcal/mol, and the most sophisticated quantum-chemical calculations[25] suggest that in the parent TMM **1** the separation is 14 kcal/mol. Even if we use the lowest estimate, the value of K, calculated (with inclusion of the appropriate statistical factor) as $K = [S]/[Tr] = (\frac{1}{3}) \cdot [\exp(-\Delta E/RT)]$, cannot be greater than 0.041. Thus, k, the mechanistic rate constant for the S + Tr reaction, would have to be >25k_2 (eq 5). Since we already know that $k_2 = 0.13k_d$ (or 0.065k_d if a departure[21-23] from Debye–Stokes–Einstein behavior is imagined), we may calculate that $k \geqslant (1.5-3)k_d$. In other words, the alleged S + Tr reaction would have to occur faster than the diffusion-controlled encounter frequency. One might argue that the use of a value of k_2 at the extreme limit permitted by the experimental error might give $k \sim k_d$, but this would be the case only if the S − Tr gap ΔE were 600 cal/mol *and no larger*. For example, even $\Delta E = 2$ kcal/mol would require $k \geqslant 414k_d$.

When the diazene **5** is pyrolyzed (>80 °C) in fluid media, dimer formation is accompanied by strong chemically induced nuclear polarization (CIDNP) of the product protons, observed as emissions in the NMR spectrum.[6a] An extension of the radical pair theory of CIDNP applied to the case of biradical dimerization predicts[26] that CIDNP will occur only if at least one of the reacting partners is a triplet. Thus, if the CIDNP-generating process is representative of the bulk of the dimer-forming process, only the reactions S + Tr or Tr + Tr need be considered for the pyrolyses in fluid media. There is of course no guarantee that the dimerization mechanism in viscous propanolic medium at low temperature is the same as in the pyrolytic case, but, if the assumption of a temperature-independent mechanism is made, the kinetic results suggest Tr + Tr as the more probable of the two CIDNP-compatible path-

ways. On the other hand, a small component of S + Tr reaction could be responsible for CIDNP but would be kinetically undetectable by our present methods.

The bicyclic hydrocarbon 5-isopropylidenebicyclo[2.1.0]-pentane (4-C) is another species that a priori might be expected to react with 4-Tr and produce dimer. It is known[6c] that pho-

tolysis of the diazene 5 at 195 K gives largely the hydrocarbon 4-C, whereas photolysis at 77 K gives mostly the triplet diyl 4-Tr. The interconversion 4-C ⇌ 4-Tr is slow at 143.6 K, since 4-C is thermally stable below 195 K,[6c] and 4-Tr gives a linear Curie plot up to 268 K.[7] Even at room temperature, disappearance of the EPR signal of 4-Tr in crystalline diazene 5 requires several minutes.[16] It is reasonable to assume that at 143.6 K, the temperature we use for photochemical generation and kinetic observation of 4-Tr, some 4-C could well be present in the reaction mixture and, in principle, could introduce a complication because the kinetics of the reaction 4-C + 4-Tr would be first order in the EPR signal. However, although we cannot exclude a small contribution of this path for dimer formation, it clearly cannot be the major mechanism, since we observe clean second-order kinetics.

Cycloaddition to Olefins. Table II shows that the second-order rate constant for capture of diyl 4 by olefins is only 10^{-3}–10^{-4} of the diffusion-controlled encounter frequency, k_d. The argument used to show that 4-S is an improbable component in the dimerization therefore cannot be applied to the cycloadditions. However, the relative reactivities suggest that the cycloadditions are true 4-Tr + olefin reactions and not reactions of the olefin with 4-S generated in a fast equilibrium from 4-Tr.

In Table V, we show the relative reactivities of olefins toward 4-Tr and 4-S at 333 K measured by competition experiments[8] and, excerpted from Table II, the relative reactivities for the three available corresponding olefins measured by the present EPR spectroscopic methods. As previously noted,[8] the singlet reactivities span a much larger range at 333 K than do the triplet reactivities. If we assume that the reactivity differences depend largely on activation enthalpy differences, we may extrapolate the singlet data from 333 to 143.6 K (last column of Table V). The decrease in temperature of course accentuates the spread in reactivities, so that one predicts, for example, that 4-S should react with dimethyl fumarate 680 times as fast as with acrylonitrile at 143.6 K. The ratio observed by EPR kinetics, however, is only 15. Extrapolation of this ratio to 333 K gives a fumarate/acrylonitrile ratio of 3.3, which considering the uncertainties in both the experimental data and the extrapolation may be considered to be in reasonably good agreement with the observed value[8] of *triplet* reactivities of 1.7.

The Arrhenius parameters $A = 10^{8.7}$ M^{-1} s^{-1} and $E_a = 6.0$ kcal/mol for the cycloaddition fall within the ranges $A = 10^{7.5\pm1.0}$ M^{-1} s^{-1} and $E_a = 6$–10 kcal/mol cited[27] as typical of reactions involving radical additions to double bonds. However, one may ask whether the Arrhenius parameters themselves can be taken as mechanistically diagnostic in the present case. In particular, can the A value be used to distinguish a stepwise olefin + 4-Tr reaction from one in which the components react to form both new bonds simultaneously?[29] An appropriate model for the latter process would be a concerted Diels–Alder reaction, for which one might expect an exceptionally low preexponential term. Using data for any given Diels–Alder process only if they cover at least four

Table V. Measured and Extrapolated Relative Rates of Cycloaddition of Olefins and 4

	triplet			singlet	
olefin[d]	143.6 K (meas[b])	333 K (ext[c] from 143.6 K)	333 K (meas[a])	333 K (meas[a])	143.6 K (ext[c] from 333 K)
(CN, NC)	4.7			180	6800
(X, X)	15	3.3	1.7	67	680
(X)			0.34	(1)	
(CN)	(1)	(1)	(1)	4	(1)

[a] By competition experiments, ref 8. [b] By EPR kinetics. [c] Assuming $\Delta\Delta S^{\ddagger} = 0$. [d] X = CO$_2$Me.

temperatures over a 30 °C range, we may derive from values in the literature[28] an average Diels–Alder $A = 10^{5.9\pm0.5}$ M^{-1} s^{-1}. This is considerably below the average radical + olefin value of $10^{7.5\pm1.0}$, but the extremes of the ranges overlap. Apparently, the major portion of the negative activation entropy of the Diels–Alder reaction is the conversion of translational to vibrational degrees of freedom that accompanies any bimolecular association.[28b] The A value $10^{8.7}$ M^{-1} s^{-1} observed for our 4-Tr + acrylonitrile reaction is at the high end (in fact slightly beyond) the typical radical + olefin range and is more than two orders of magnitude beyond the high end of the concerted Diels–Alder range. Although the overlap of the "typical" radical addition and Diels–Alder ranges makes the argument less than compelling, it is nevertheless tempting to conclude that the 4-Tr + acrylonitrile reaction is a true, stepwise radical addition process. This is, of course, entirely consistent with the previous conclusions[6b,8,9] based upon stereorandomization in the triplet additions to dimethyl maleate and dimethyl fumarate.

Summary

The EPR-monitored dimerization of 4-Tr is a second-order reaction which most probably involves 4-Tr + 4-Tr rather than 4-Tr + 4-S combination, since the latter reaction would have to be faster than the diffusion-controlled encounter frequency to fit simultaneously the observed rate constant and the low concentration of 4-S permitted by the linearity of the EPR Curie plot. The EPR-monitored cycloaddition 4-Tr + olefin again is a true triplet reaction rather than 4-S + olefin, because the reactivity trends of the olefins parallel those found in direct competition experiments, where the 4-Tr and 4-S mechanisms have been dissected. The cycloaddition probably occurs one bond at a time.

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15N Nuclear Magnetic Resonance Spectroscopy. Products and Rearrangements in the Reaction of p-Toluenesulfonyl Azide-3-15N with the Sodium Salt of p-Toluenesulfonamide. An in Situ 15N NMR Study[1]

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Abstract: The formation of isotope-scrambled 15N-labeled diazocyclopentadiene from the reaction of p-toluenesulfonyl azide-3-15N (1-3-15N) with cyclopentadiene is caused by one of the reaction products (p-toluenesulfonamide anion) which is quite effective for scrambling 1-3-15N. A number of concurrent reactions of 1-3-15N with the sodium salt of p-toluenesulfonamide in dimethyl sulfoxide were followed by 15N NMR. 1-2-15N is formed as a result of a degenerate diazo transfer by 1-3-15N to p-toluenesulfonamide anion. p-Toluenesulfonamide anion also reacts with 1-3-15N to give di-p-toluenesulfonamide and azide ion. The 15N-labeled azide ion exchanges with 1 to give 1-1-15N. 1 also reacts with azide ion, yielding dinitrogen and p-toluenesulfinate anion. The sulfinate salt reacts readily and reversibly with 1 to give 1,3-di-p-toluenesulfontriazene anion, which provides another pathway for interconversion of 1-3-15N and 1-1-15N.

Introduction

p-Toluenesulfonyl azide (1) is a highly versatile and useful reagent[2] which, depending on the conditions, can behave as an electrophile, nucleophile, a 1,3 dipole,[3] or source of p-toluenesulfonylnitrene.[3] As an electrophile, 1 resembles aryldiazonium compounds. The electrophilic nature of N3 (the terminal nitrogen) can be rationalized by the resonance structure 1b and is exploited in the well-known diazo[4] and azido[5]
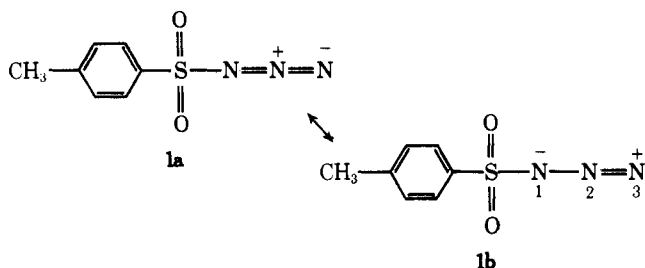
transfers to active methylene groups. These transfers are believed to occur by the mechanistic steps of Scheme I.[4,6] The carbanion formed by ionization of the substrate attacks the

electrophilic N3 of 1 to give a triazene adduct, 2. Such triazenes have occasionally been isolated and characterized.[6,7] When the anion has an α hydrogen (R' = H), 2 tautomerizes to 3, and 3 then decomposes to yield a diazo compound and the resonance-stabilized p-toluenesulfonamide anion. When the anion has no α hydrogen (R' ≠ H), 2 decomposes directly to give an azido compound and p-toluenesulfinate anion. Both diazo and azido transfers by 1 have, in recent years, been extended to a wide variety of nitrogen anions, primarily by Anselme and co-workers.[8,9]

Recently, 1 labeled at N3 with 15N was used to synthesize labeled diazocyclopentadiene, and, contrary to expectations, the 15N NMR spectrum of the product showed that, in addition to 4, about 5% of 5 was formed.[10] The discovery by several research groups[11,12] that 1 transfers a diazo group to the magnesium salts of primary amines by the process of eq 2[11] suggests that 1-3-15N might be scrambled by the p-toluenesulfonamide anion formed in eq 1 as the result of a degenerate diazo-transfer reaction.

In this paper, we give an account of the reactions of 1-3-15N with the sodium salt of p-toluenesulfonamide (generated in situ from excess p-toluenesulfonamide) in dimethyl sulfoxide,