and T_r, respectively.[42] Reduced temperatures are defined by

$$T_{r(L)} = (T - T_{mp(L)})/(T_{bp(L)} - T_{mp(L)}) \qquad (22)$$

where T is the experimental temperature and $T_{mp(L)}$ and $T_{bp(L)}$ are the melting point and boiling point of the solute or solvent, respectively. Resulting correction terms were assumed to be additive and to be related to specific interactions between solvent–solvent and solvent–solute molecules.[42] The full expression for f_t is accordingly given by

$$f_t = (0.16 + 0.4r/r_L)(0.9 + 0.4T_{rL} - 0.25T_r) \qquad (23)$$

Use of the reduced temperature term in eq 23 in an attempt to extract solvent- and solute-independent f_t's improves the fit to eq 20 marginally, reducing the average deviation from ~12 to ~8%.

Use of eq 20 to predict f_t's has been advocated by Alwattar, Lumb, and Birks.[2c] D's are then calculated from

$$D = kT/f_t\zeta = kT/\zeta_\mu \qquad (24)$$

which is eq 8 with Stokes' friction coefficient ζ replaced by the microfriction coefficient ζ_μ. It was proposed further that the stick limit of eq 9, $\zeta = 6\pi\eta r$, be replaced by the slip limit, $\zeta = 4\pi\eta r$, when $r/r_L < 1$.[2c] Though this suggestion may have merit, it neglects the fact that eq 20 is based on f_t's calculated by using the stick limit for ζ, eq 19, regardless of the r/r_L value, $0.72 \leq r/r_L \leq 1.84$.[42] Thus, the excellent agreement between experimental D's for several solutes in n-hexadecane, $0.60 \leq r/r_L \leq 0.80$, and D's predicted by eq 24 with $\zeta = 4\pi\eta r^{2c}$ is probably fortuitous.

Schuh and Fischer estimated full microfriction factors, f_t(full), and truncated microfriction factors, f_t(trunc), for the *tert*-butyl radical, t-Bu, with eq 23 and 20, respectively, using isobutane or n-butane as models for t-Bu. D's were calculated from eq 24 with $\zeta = 6\pi\eta r$ for all r/r_L consistent with the definition of the empirical f_t's. The contribution of the reduced temperature term in eq 23 increases as the molecular weight of the solvent is increased. This is evident in the series of n-alkane solvents, C_7 to C_{16}, where f_t(trunc)/f_t(full) increases from 1.2 to 1.7. For the higher molecular weight alkanes only f_t(full) gives D's in good agreement with values calculated by other empirical methods. Consequently, f_t(full) was used generally to calculate t-Bu encounter rate constants.[24] It should be noted that because the reduced temperature term in eq 19 was developed from diffusion coefficients for relatively low boiling point solutes and solvents (e.g., n-octane was the longest chain n-alkane solvent represented in the data set) to compensate marginally for rather small deviations from eq 20 ($\leq 25\%$), its use with higher molecular weight solvents or solutes represents a risky extrapolation.

Assuming that k_{obsd} and k_t are fully diffusion controlled, but including the spin-statistical factor, ϕ, in k_t, gives

$$\frac{k_{obsd}}{k_t} = \left(\frac{1}{\phi}\right)\left(\frac{\rho_{et}}{\rho_t}\right)\left(\frac{D_{et}}{D_t}\right) \qquad (25)$$

where ρ_{et} and ρ_t are encounter radii for triplet excitation transfer and radical self-termination, respectively, and D_{et} and D_t are the corresponding diffusion coefficients, eq 7. Assuming ρ's and D's equal to the sums of the molecular radii and the diffusion coefficients of the reactants, respectively, and solving eq 19, 24, and 25 for ϕ^{-1} gives

$$\phi^{-1} = \left(\frac{k_{obsd}}{k_t}\right)\left(\frac{4r_{Az}r_{In}}{r_{Az} + r_{In}}\right)\left(\frac{f_t^{Az}f_t^{In}}{f_t^{t-Bu}(f_t^{Az}r_{Az} + f_t^{In}r_{In})}\right) \qquad (26)$$

where f_t^{t-Bu}, f_t^{Az}, and f_t^{In} are translational microfriction coefficients for t-Bu, Az, and In, respectively, and the molecular radii, r_x, of the reactants are obtained from the molar volumes, V_x in cm^3, using

$$r_x = (3000V_x\chi/4\pi N)^{1/3} \qquad (27)$$

where $\chi = 0.74$ is the space-filling factor for closest packed spheres.[2c,24,42]

Calculated f_t(trunc), f_t(full), and corresponding ϕ^{-1} values are listed in Table VII. Molecular radii were not adjusted for temperature changes. Since r_x is proportional to $d^{-1/3}$, it is not very sensitive to density changes. In any case, such changes should cancel out in r/r_L ratios, and f_t(trunc) (eq 20) should not vary significantly with temperature. Similarly, f_t(full) is nearly temperature independent, owing to complementary changes in solvent and solute reduced temperature terms in eq 23. The large values of ϕ^{-1}, 5.7–8.3, obtained using f_t(full) are not considered trustworthy. As pointed out above, reduced temperature corrections for high molecular weight solvent or solute molecules fall well outside the empirical $\Delta f_t/f_t$ range which served as basis for eq 19, e.g., for In $0.44 \leq \Delta f_t/f_t \leq 0.61$. On the other hand, the ϕ^{-1} range, 3.5–5.0, obtained using f_t(trunc) is remarkably close to 4, the proposed spin-statistical value. As a further test of the conclusion that f_t(trunc) in eq 26 is much more likely to give correct predictions, f_t values were intrapolated directly from a plot of D_{exptl} in toluene vs. r/r_L.[42] The microfriction factors obtained (Table VII) are almost identical with f_t's calculated with only the solvent reduced temperature correction in eq 23. The predicted range of ϕ^{-1}, 3.6–3.9, is well within experimental error of 4, and in excellent agreement with the range predicted using f_t(trunc).

Carbanion Photochemistry. 3. Electron Transfer and Radical-Anion Control in the Photochemistry of Triphenylmethyl Anion[1]

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Abstract: On the basis of concentration and competition studies, the photomethylation of triphenylmethyl anion in dimethyl sulfoxide is shown to involve the reaction of methyl radical with triphenylmethyl anion to yield the radical anions of 1,1,1-triphenylethane and 3-(diphenylmethylene)-6-methyl-1,4-cyclohexadiene. However, there are no chain-carrying steps as there are for typical $S_{RN}1$ reactions. The intervention of radical anions produces the unconventional product of para alkylation, but the reaction is dominated by the bond strength of the newly formed bond as indexed by pK_a.

Recently we observed the facile photomethylation of resonance stabilized carbanions in dimethyl sulfoxide.[2] Our subsequent work

in this area has led us to the conviction that the overwhelming reaction pathway is electron transfer, despite some rather for-
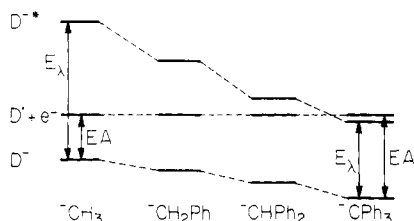
Figure 1. Effect of phenyl substitution.

midable energy constraints. The relatively low-energy light employed and the obvious applications to fundamental studies in solar energy conversion via electron photoejection have prompted us to narrow our scope to the photochemistry of triphenylmethyl anion itself, the results of which we now present.

Background. Enolates and other carbanions often undergo dimerization reactions by pathways which are suggestive of electron transfer.[3,4] The reason for this pathway is clear, if not always stated: associated with a negatively charged species is an excess of electron–electron repulsion terms over nuclear attraction terms; that is, the valence electrons are shielded from the nucleus. Thus photoexcitation easily places a carbanion in a state of excess energy relative to the state corresponding to neutral plus a free electron, and the species autodetaches. The crucial parameter determining whether a species will autodetach, then, is the relative magnitude of the excitation energy E_λ and the electron affinity (EA) of the neutral.

Substition by phenyl increases the electron affinity of a radical center at the expense of the excitation energy. Thus the electron affinity of benzyl is at least 7 kcal greater than methyl,[5] while λ_{max} for triphenylmethyl anion is red-shifted by 45 nm relative to diphenylmethyl anion,[6] corresponding to a decrease in E_λ of 6 kcal. Figure 1 illustrates these opposing effects.
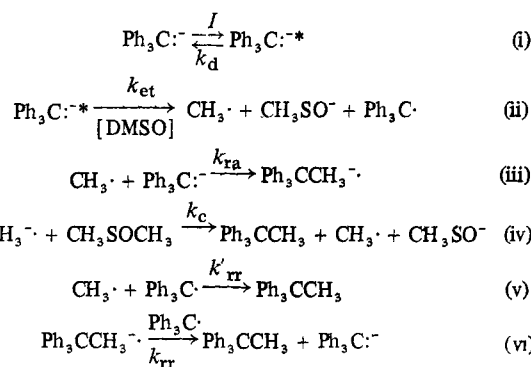
By irradiating triphenylmethyl anion in dimethyl sulfoxide, we anticipated that electron transfer would be circumvented. Me_2SO is resistant to reduction at potentials less negative than -3.0 V vs. SCE,[7] while the reduction potential of triphenylmethyl radical is reported as -1.20 V vs. SCE.[8] Thus the energy required for the reduction of Me_2SO by trityl anion corresponding to a potential of 1.8 V is 41 kcal. As a minimum this requires that all the available excited state energy (the onset of absorption of some carbanions is 650 nm) is incorporated in the electron transfer.

Results. Preliminary Photolyses. The triphenylmethyl anion underwent smooth photomethylation under the influence of 0.1 M K_2CrO_4 filtered 450-W Hanovia light to produce two products, 1,1,1-triphenylethane (**1**) and 1,1-diphenyl-1-*p*-tolylethane (**2**) (see eq 1). The 60% yield is based upon material isolated by extraction and recrystallization. Gas chromatographic yields averaged 87%.

1 (50%)   **2 (8%)**   (1)
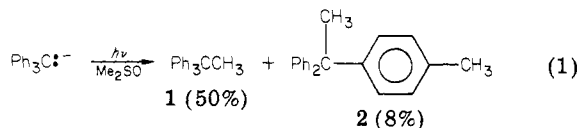
The presence of para-methylated product **2** suggested the intervention of diphenyl-*p*-tolylmethane (**3**) which was confirmed by irradiation to lower conversions, chromatographic detection, and comparison with independently prepared material. The di-

Scheme I

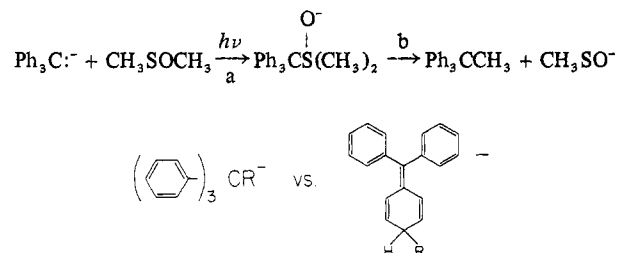$$Ph_3C^{:-} \underset{k_d}{\overset{I}{\rightleftharpoons}} Ph_3C^{:-*} \qquad (i)$$

$$Ph_3C^{:-*} \xrightarrow[\text{[DMSO]}]{k_{et}} CH_3\cdot + CH_3SO^- + Ph_3C\cdot \qquad (ii)$$

$$CH_3\cdot + Ph_3C^{:-} \xrightarrow{k_{ra}} Ph_3CCH_3^{-\cdot} \qquad (iii)$$

$$Ph_3CCH_3^{-\cdot} + CH_3SOCH_3 \xrightarrow{k_c} Ph_3CCH_3 + CH_3\cdot + CH_3SO^- \quad (iv)$$

$$CH_3\cdot + Ph_3C\cdot \xrightarrow{k'_{rr}} Ph_3CCH_3 \qquad (v)$$

$$Ph_3CCH_3^{-\cdot} \xrightarrow[k_{rr}]{Ph_3C\cdot} Ph_3CCH_3 + Ph_3C^{:-} \qquad (vi)$$

Scheme II

$$Ph_3C^{:-} + CH_3SOCH_3 \xrightarrow[a]{h\nu} \overset{O^-}{\underset{}{Ph_3CS(CH_3)_2}} \xrightarrow{b} Ph_3CCH_3 + CH_3SO^-$$

Figure 2.

methylated product **2** was also prepared independently.

Mechanistic Investigations. One-Electron vs. Two-Electron Processes. Mechanisms for the photomethylation can be grouped into two types, those involving electron transfer and those involving two-electron processes (nucleophilic attack or exciplex formation). The former is exemplified by the $S_{RN}1$ mechanism,[9] given here as Scheme I. The latter process is represented by the exciplex mechanism, Scheme II. Although other mechanisms involving prior electron transfer are possible, the most clearly distinguishing feature of these two mechanisms is the concertedness of the carbon–sulfur bond breaking and carbon–carbon bond making in step b of Scheme II. In contrast, Scheme I requires carbon–sulfur bond breaking as a first step.[10] We note that decomposition of σ-sulfuranes, the closest molecular analogy to the presumed intermediate for Scheme II, proceeds with migration of the group best able to sustain a negative charge.[11] Thus irradiation in the presence of an unsymmetrical sulfoxide should lead to different products for each mechanism, since Scheme I would transfer the group having the weakest carbon–sulfur bond. Such a requirement is satisfied with methyl phenyl sulfoxide.

The irradiation of triphenylmethyl anion in tetrahydrofuran containing methyl phenyl sulfoxide led to a hydrocarbon product mixture essentially indistinguishable from that in dimethyl sulfoxide (see eq 2). No traces of tetraphenylmethane or diphenyllyldiphenylmethane were detected.[12] This result strongly implicates carbon–sulfur bond breaking as the critical step in determining product formation.

The Role of Radical–Anion vs. Radical–Radical Recombination. The previous experiment established dimethyl sulfoxide decom-

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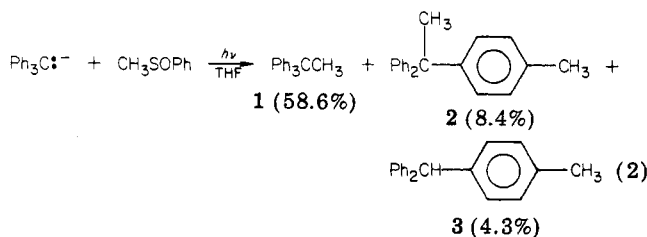(7) Jones, J. L.; Fritsche, H. A., Jr. *J. Electroanal. Chem.* **1966**, *12*, 334.

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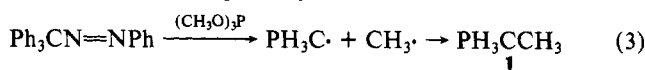
(10) (a) Dimethyl sulfoxide is known to produce methyl radicals upon electron capture during radiolysis.[10b] Whether the radical anion of Me_2SO is formed followed by dissociation or whether carbon–sulfur bond cleavage is concerted with electron transfer is not known for these conditions. (b) Meissner, G.; Henglein, A.; Beck, G. Z. *Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1967**, *22B*, 13.

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(12) That the phenyl moiety can be transferred under forcing conditions was proved by carrying out the irradiation in the presence of diphenyl sulfoxide in tetrahydrofuran, which led to the formation of tetraphenylmethane.

$$\text{Ph}_3\text{C:}^- + \text{CH}_3\text{SOPh} \xrightarrow[\text{THF}]{h\nu} \text{Ph}_3\text{CCH}_3 + \text{Ph}_2\overset{\overset{\displaystyle CH_3}{|}}{\text{C}}\!-\!\!\langle\bigcirc\rangle\!\!-\!\text{CH}_3 +$$

$$\mathbf{1}\ (58.6\%) \qquad\qquad \mathbf{2}\ (8.4\%)$$

$$\text{Ph}_2\text{CH}\!-\!\!\langle\bigcirc\rangle\!\!-\!\text{CH}_3 \quad (2)$$

$$\mathbf{3}\ (4.3\%)$$

position, either via its radical anion or via dissociative electron transfer, as the key initial step upon photoexcitation. Our next goal was determining the fate of methyl radicals so generated and the mechanistic pathway leading to products. As outlined in Scheme I, two product-forming pathways are possible. One involves methyl adding electrophilically to trityl anion to generate product radical anion (step iii); the other involves methyl radical adding to trityl radical generated in the initial electron-transfer step to form final product directly (step v). In this regard we were fortunate to have additional products of para alkylation (diphenyltolylmethane (**3**) and diphenyltolylethane (**2**)) which were reminiscent of products obtained from photoarylation of trityl anion in the presence of bromobenzene.[13] We had speculated that the radical–anion pathway should exhibit a greater preference for the para product than the neutral pathway because of the greater delocalization in the (diphenylmethylene)cyclohexadiene system, which is the required intermediate in formation of **2** and **3** (see Figure 2). Conversely, the radical–radical pathway should lead to the single product 1,1,1-triphenylethane (**1**). This is in fact the case. Bentrude and Fu reported that methyl radical generated from trimethyl phosphite during the decomposition of phenylazotriphenylmethane combines with trityl radical to yield exclusively the α product **1**[14] (see eq 3), and we confirmed this result, excluding the presence of diphenyl-*p*-tolylmethane. Thus, radical–radical recombination cannot account for all of the product formed, and we attribute the presence of para-alkylated products to the radical–anion pathway.

$$\text{Ph}_3\text{CN}\!=\!\!=\!\text{NPh} \xrightarrow{(\text{CH}_3\text{O})_3\text{P}} \text{PH}_3\text{C·} + \text{CH}_3\text{·} \rightarrow \underset{\mathbf{1}}{\text{PH}_3\text{CCH}_3} \quad (3)$$
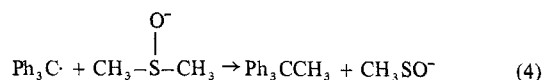
Although radical–radical recombination cannot account for all of the products, it is still possible for this pathway to be responsible for the major reaction product **1**. Our next goal, then, was to determine the relative importance of the two pathways. We note that the radical–radical pathway is monomolecular in triphenylmethyl anion. That is, the triphenylmethyl moiety undergoing irradiation is also the one incorporated into product. The radical–anion pathway, however, involves methyl radical combining with trityl anion, and the rate for this pathway will have a linear dependence upon anion concentration. To the extent step iii and step v are involved simultaneously, the ratio of para-alkylated products **2** and **3** to α-alkylated product **1** should be dependent upon the concentration of trityl anion (see Figure 3).

We irradiated trityl anion in Me₂SO at different initial concentrations and observed the ratios of α to para products formed. We included dimethylated product **2** with monomethylated product **3** because **2** is the direct product of **3**. The results are listed in Table I. Within experimental error, the ratio of para to α products is constant. Thus we conclude that both products are formed at the same step, and since we have concluded that the radical–anion pathway must be involved in part of the mechanism, it must represent the dominant reaction pathway.

Results and Discussion. Competitive Trapping of Methyl Radical by the Radical–Anion Pathway. Although the evidence presented thus far clearly establishes electron transfer as the key step in the process and suggests radical–radical anion combination as the bond-forming step, we must rule out the intervention of rate-limiting electron transfer followed by a fast methyl transfer, the

S$_H$2 mechanism (eq 4). We note that Scheme I requires that

$$\text{Ph}_3\text{C·} + \text{CH}_3\!-\!\!\overset{\overset{\displaystyle O^-}{|}}{\text{S}}\!-\!\text{CH}_3 \rightarrow \text{Ph}_3\text{CCH}_3 + \text{CH}_3\text{SO}^- \quad (4)$$

the same products be formed regardless of the source of methyl radical, while the S$_H$2 modification does not. Thus irradiation of one anion which promotes alkylation of another is prima facie evidence for the intervention of Scheme I. Competitive trapping experiments confirmed this hypothesis. When we irradiated equimolar mixtures of triphenylmethyl anion and diphenylyldiphenylmethyl anion at wavelengths such that the diphenylyldiphenylmethyl anion absorbed ca. 90% of the light, triphenylmethyl anion was alkylated to the extent of 85% of the product mixture. We therefore conclude that carbon–carbon bond formation is not concerted with carbon–sulfur bond breaking and that the reaction pathway is dominated by the reaction of methyl radical with triphenylmethyl anion.

We have reported on the unexpected preference for alkylation of the more basic triphenylmethyl anion despite lesser stability of the radical–anion product relative to the diphenylyldiphenylmethyl anion, and we have attributed this effect to a kinetic preference for formation of the more stable bond as measured by pK_a.[1] We note with interest the large percentage of bis-alkylated product **2** arising from alkylation of diphenyltolylmethane via equilibration to the conjugate base, despite the fact that **3** is an inherently weaker acid. Again, the pK_a effect predominates.

Results and Discussion. The Role of Chain Processes. Although S$_{RN}$1 reactions typically involve chain processes, the quantum yield of disappearance of trityl anion upon irradiation was measured and found to be 0.06, strongly suggesting that a chain process is not involved.[15] However, quantum yields below unity are not necessarily compelling evidence for such a conclusion. More conclusive are anion concentration dependent quantum yields. For a chain process, the limiting quantum yield is given by eq 5 (see

$$\Phi_r = k_{ra}[\text{T}^-]\left[\frac{k_{et}}{(k_d + k_{et})Ik_{rr}}\right]^{1/2} \quad (5)$$

Appendix), where k_{ra} is the rate constant for radical–anion combination (step iii), k_{et} is the pseudo-first-order rate constant for electron transfer (step ii) and includes a [Me₂SO] factor, k_c is the rate constant for the chain-carrying step (step iv), k_d is the rate constant for excited-state decay in the absence of electron transfer, k_{rr} is the rate constant for radical–radical recombination (step v), I is the rate of light absorption (step i), and [T$^-$] is the concentration of the trityl anion. The limiting quantum yield for the nonchain process ($k_c \simeq 0$) is given by more standard kinetics (see eq 6).

$$\Phi_r = \frac{k_{et}}{k_{et} + k_d} \quad (6)$$

By simultaneously monitoring light output and triphenylethane product formation, we obtained the plot shown in Figure 4. Within experimental error, the slope over 1 half-life of trityl anion is linear, giving a correlation coefficient of 0.999. The linearity of this plot and the constancy of the quantum yield clearly exclude the appreciable intervention of a chain mechanism.

Since the observed kinetics are rate limited by electron transfer to dimethyl sulfoxide, we have no information about the value of the other rate constants. Specifically, the last step of the mechanism must involve electron transfer from a radical anion to yield a neutral product. However, since the yields of products approach 90%, we conclude that the majority of the final electron transfer involves triphenylmethyl radical (step vi). Any other pathway would necessarily drive the yield to below 50%, since two

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(15) Actually this is the quantum yield of disappearance of triphenylmethane. To the extent that triphenylmethane is a photochemical product of triphenylmethyl anion, for instance, by hydrogen abstraction, the true quantum yield for triphenylmethyl anion disappearance will be increased by a compensating amount.
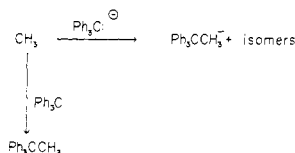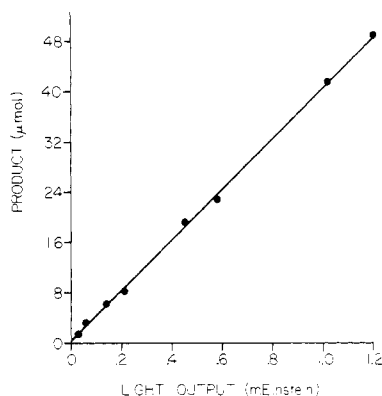
Figure 3. Competitive radical vs. anion capture.

Figure 4. Triphenylethane quantum yield data.

Table I. Effects of Carbanion Concentration

Ph_3C:− concn, M	yields of methylated products, %			
	1	3	2	p/α, %
0.138	59.8	7.0	9.8	28.1%
0.050	64.2	16.0	3.8	30.9%
0.033	65.2	17.7	2.5	31.1%

molecules of triphenylmethyl anion would be consumed for each molecule of product formed.

Discussion. Free-Radical Quenching Studies. Although the mechanistic and kinetic evidence presented here constitutes a compelling argument for the nonchain free-radical mechanism, some inconsistencies remain, of which the most glaring is the failure of typical methyl radical scavengers to quench the reaction. Thus neither cyclohexane nor toluene inhibited the formation of the alkylated product. However, we should point out that scavenging of methyl radicals by hydrogen atom donors is an activation energy-controlled process[16] which may not be observable in the presence of a process of lower activation energy. Since at present we do not have the activation energies for the reactions of radicals with carbanions, we cannot predict whether methyl radicals should have been scavenged under these conditions. Therefore we chose to investigate the photolysis in the presence of spin traps which efficiently trap methyl radical.[17]

Addition of *N*-phenyl-*tert*-butylnitrone (PBN)[17b] to solutions of triphenylmethyl anion in Me_2SO led to immediate loss of the anion prior to irradiation, presumably via a ground-state electron transfer, and precluded its use as a methyl trap. Conversely, addition of di-*tert*-butylnitroxide (DBN)[17a] to triphenylmethyl anion produced no loss of color or anion destruction. Irradiation of such solutions led to contrasting results which depended upon the concentration of DBN. At low concentration, yields of product declined substantially, consistent with the interception of methyl radicals by the nitroxide. At high concentration of DBN, the photochemistry was quenched completely, and solutions were inert to photolysis under conditions which would have converted several equivalents of anion in the absence of the spin trap. This result is consistent with quenching of the excited state of anion by direct reversible electron transfer to DBN. In other words, at low concentrations step iii of Scheme I is diverted and at high concentrations step i is quenched.

Conclusions

The photochemistry of triphenylmethyl anion provides a unique vehicle for investigating step by step the consequences of interaction of light with a negatively charged species. We have discovered that electron ejection is still the dominant pathway, despite the relatively high potential required. Electron transfer to Me_2SO leads to the formation of methyl radicals, which combine with other anions at a rate at least partially dependent on the pK_a of the corresponding carbon acid.[1] The resulting radical anion does not carry on a chain process but ultimately restores an electron to the triphenylmethyl radical. We have the important result that excited triphenylmethyl anion can promote a chemical reaction in another substrate.

The photochemistry of triphenylmethyl anions is characterized by a remarkable absence of side products, i.e., dimers and free-radical chain products, characteristic of ground-state methods. The radicals and radical anions produced under the latter conditions are formed in relatively high concentrations resulting in relatively facile biradical reaction pathways. Under photopromoted conditions, not more than a low steady state of methyl radical is produced, so that radical–radical reactions do not contribute in the product-controlling steps.

The reaction of radicals with anions is clearly a phenomenon that merits further exploration. On the one hand, the exothermicity of the reaction is not nearly as great as for radical–radical reactions, so that product formation is not diffusion controlled. On the other hand, the activation energies required are less than for other types of radical–induced reactions such as hydrogen abstraction. We are currently exploring these kinetic boundaries to provide an estimate for the actual activation energies of this process in order to relate these to the structure and properties of resonance-stabilized anions themselves.

Further important questions remain to be answered, e.g., what is the nature of the photoejecting state or how reversible is electron transfer to Me_2SO. However, we now understand the crucial steps in product formation. Understanding how structural changes affect these steps is our next goal.

Experimental Section

Melting points were taken on a hot-stage apparatus and are uncorrected. Nuclear magnetic resonance spectra were obtained on a Varian T-60 or HFT-80 spectrometer. Solutions of anions were prepared and irradiated as described earlier.[1]

Materials. Triphenylmethane was obtained from Aldrich Chemical Co. and was either used as received or recrystallized from methanol. 4-Tolyldiphenylmethane[8] was obtained by boiling formic acid treatment of 4-tolyldiphenylcarbinol, which in turn was obtained from 4-tolylmagnesium bromide treatment of benzophenone. Diphenylyldiphenylmethane was obtained by the method of Bordwell.[18] 1-(4-Tolyl)-1,1-diphenylethane and 1,1,1-triphenylethane were prepared as previously reported.[1]

Chromatography. Gas chromatographic analysis was performed on a Varian 3700 gas chromatograph by using a 3-m column of 2% OV-101 on Chromosorb G. High-pressure liquid chromatography was performed on a 25 cm × 2 mm column of Porasil-ODS on a Laboratory Data Control modular system incorporating a variable wavelength detector set at 238 nm and using 60% acetonitrile–water as eluant.

Quantum Yields. Quantum yields were determined on a chemists optical bench essentially identical with that described by Zimmerman.[19] Irradiations of triphenylmethyl anion were carried out at 550 nm by using a Bausch and Lomb super high-pressure mercury arc lamp equipped with a high-intensity grating monochromator. Light output was monitored by an integrating photometer[20] using an EG and G HUV-1000B operational amplifier–photodiode combination as a detector. The detector was mounted at right angles to the light beam so as to capture the light reflected by a quartz plate beam splitter placed at 45° in the light beam. For maximum sensitivity and linearity, the photodiode was run in the photovoltaic mode. Calibration was carried out with a Scientech Model

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36-0001 Disc Calorimeter. Analysis of product formation was by gas chromatography.

In the run represented by Figure 4, 49.2 mg of triphenylmethane in 48 mL of dimethyl sulfoxide were reacted with 2 mL of 0.368 M potassium dimsyl. The solution was irradiated at 550 nm, and aliquots were removed at 1, 2, 4, 7, 17, and 24 h. Calibrated volumes were injected on the gas chromatograph, and the detector response was standardized by using authentic samples. The detector counts were converted to light output in einsteins, and the product vs. light output gave the plot in Figure 4. Least-squares treatment of the points gave a quantum yield of triphenylethane appearance of 0.0406 ± 0.0003. Similar treatment of starting material gave a quantum yield of disappearance of 0.0658 ± 0.004.[22,23]

Concentration Dependent Runs. To 2 g of triphenylmethane in Me₂SO was added 0.138 M potassium dimsyl in the amount indicated. The initial amount of Me₂SO added was precalculated to bring the total volume of solution to 50 mL. The solution was irradiated until the red disappeared (4–20 h). Triphenylethylene (ca. 0.5 g) was added as an internal standard, and the solutions were analyzed by gas chromatography. Calibration of the detector response was performed by using a standard solution of authentic materials. The amounts of materials introduced and products produced were as follows, with percentages based upon initial base concentration.

Run 1: Triphenylmethane, 1.96 g; potassium dimsyl, 50 mL; triphenylethylene, 0.453 g. Products: triphenylethane, 1.07 g, 59.8%; 4-tolyldiphenylmethane, 0.125 g, 7.0%; 4-tolyldiphenylethane, 0.184 g, 9.8%.

Run 2: Triphenylmethane, 2.12 g; potassium dimsyl, 18 mL; triphenylethylene, 0.196 g. Products: triphenylethane, 0.412 g, 64.2%; 4-tolyldiphenylmethane, 0.103 g, 16.0%; 4-tolyldiphenylethane, 0.259 g, 3.8%.

Run 3: Triphenylmethane, 1.82 g; potassium dimsyl, 12.1 mL; triphenylethylene, 0.107 g. Products: triphenylethane, 0.283 g, 65.2%; 4-tolyldiphenylmethane, 0.0766 g, 17.7%; 4-tolyldiphenylethane, 11.6 g, 2.5%.

Irradiation of Triphenylmethyl Anion in Methyl Phenyl Sulfoxide. A solution of potassium phenylsulfinylmethide was prepared as follows: a sample of dry potassium hydride in argon was prepared by washing 3.0 mL of 20% potassium hydride with pentane, using the procedure outlined for potassium dimsyl. This amount of potassium hydride was calculated on the basis of previous experiments to yield 8.3 mmol of active potassium hydride. A solution of 25 mL of dry tetrahydrofuran containing 3.0 g (21.0 mmol) of methyl phenyl sulfoxide was added slowly so as to control frothing. The resulting solution was degassed by cooling to below 0 °C and evacuating the vessel to <0.1 torr. Argon was reintroduced, and the solution was added to the previously degassed photolysis chamber containing 2.73 g (11.2 mmol) of triphenylmethane. The red solution was irradiated for 12 h. The solution was diluted with water and extracted with ether. Analysis of the extract by gas chromatography and nuclear magnetic resonance spectroscopy showed the presence of triphenylmethane (0.406 g, 1.66 mmol), 1,1,1-triphenylethane (1.69 g, 6.55 mmol), 1-tolyl-1,1-diphenylmethane (0.124 g, 0.48 mmol), and 1-(4-tolyl)-1,1-diphenylethane (0.255 g, 0.94 mmol). Conversely, comparison with authentic samples showed the absence of tetraphenylmethane or diphenylyldiphenylmethane within the limits of detection, i.e., <0.01 g.

Low-Conversion Irradiation of Triphenylmethyl Anion. A solution of triphenylmethyl anion prepared from 1.66 g (6.79 mmol) of triphenylmethane, 20 mL (4.0 mmol) of 0.2 M dimsylpotassium in dimethyl sulfoxide, and 30 mL of dimethyl sulfoxide was irradiated for 7 h. The reaction was quenched with water and analyzed by gas chromatography, which indicated ca. 10% conversion to products. Multiple column temperature studies using independently prepared material indicated the presence of 2% tolyldiphenylmethane (3). The reaction mixture was also chromatographed on an analytical high-pressure chromatograph. Again, comparison with independently prepared material indicated the presence of 2% tolyldiphenylmethane. Attempts at purification by using alumina or silica gel chromatography yielded only enrichment of the para methylated product in the triphenylmethane fraction.

Photolyses in the Presence of Hydrogen Atom Donors. Solutions of triphenylmethyl anion (1.0 mmol in 50 mL of Me₂SO) were prepared by using a twofold excess of dimsylpotassium. A 5-mL portion of either

cyclohexane or toluene was added. The red solution was stirred for 30 min and then irradiated for 24 h. The solution was quenched with 2 mL of water and then analyzed by gas chromatography. The products formed were indistinguishable in composition and amounts from those run in the absence of hydrogen atom donor. In particular, 1,1,1,2-tetraphenylethane, the presumed product of reaction of benzyl radical with triphenylmethyl anion, was excluded as a product from photolysis in the presence of toluene by comparison with independently prepared material.

Irradiation of Triphenylmethyl Anion with Di-*tert*-butyl nitroxide (DBN). Run 1. To a solution of triphenylmethyl anion prepared from 0.271 g (1.11 mmol) of triphenylmethane, 10 mL (3.0 mmol) of 0.30 M potassium dimsyl in dimethyl sulfoxide, and 40 mL of dimethyl sulfoxide was added 0.199 g (1.38 mmol) of DBN. The solution was irradiated for 24 h by using a Hanovia 450 W medium-pressure mercury arc lamp and a 0.1 M K₂CrO₄ solution filter. The reaction mixture was quenched with 2 mL of water, triphenylethylene was added as an internal standard, and the products were quantitated by gas chromatography. The products were as follows: triphenylmethane, 43.1 mg (0.177 mmol); 1,1,1-triphenylethane, 119.1 mg (0.462 mmol); tolyldiphenylmethane (3), 9.3 mg (0.036 mmol); 1-tolyl-1,1-diphenylethane (2), 19.9 mg (0.073 mmol). Thus the yield of products based upon starting anion is 58% (cf. 87%).

Run 2. A solution of triphenyl anion was prepared by using 0.238 g (0.975 mmol) of triphenylmethane, 5 mL (1.5 mmol) of 0.30 M potassium dimsyl, 0.401 g (2.78 mmol) of DBN, and 15 mL of dimethyl sulfoxide. Thus the concentration of DBN was fivefold that of run 1. Irradiation for 40 h under the same conditions as run 1 showed no loss of color. The reaction mixture was quenched with 2 mL of water, and triphenylethylene was added as an internal standard. Within the limits of detection (<0.1%), no methylated products were produced. The yield of triphenylmethane was 0.218 g (95%).

Appendix

Kinetic Treatment of Data. To reduce the complexity of the derivation, for the kinetics of product formation in Scheme I, it is useful to use the shorthand notation in eq a–d. Using the

$$[Ph_3C:^-] = [T^-] \tag{a}$$

$$[Ph_3C\cdot] = [T\cdot] \tag{b}$$

$$[Ph_3CCH_3] = [P] \tag{c}$$

$$[Ph_3CCH_3\cdot^-] = [P^-\cdot] \tag{d}$$

steady-state approximation, we are able to write the expressions (e)–(h) for the rates of formation of the transients.

$$\frac{dT^-*}{dt} = I - (k_d + k_{et})[T^-*] = 0 \tag{e}$$

$$\frac{dCH_3}{dt} = k_{et}[T^-*] + k_c[P^-\cdot] - k_{ra}[CH_3][T^-] - k_{rr}[CH_3][T\cdot] = 0 \tag{f}$$

$$\frac{dT\cdot}{dt} = k_{et}[T^-*] - k_{rr}[T\cdot][P^-\cdot] - k'_{rr}[CH_3][T\cdot] = 0 \tag{g}$$

$$\frac{dP^-\cdot}{dt} = k_{ra}[CH_3][T^-] - k_c[P^-\cdot] - k_{rr}[P^-\cdot][T\cdot] = 0 \tag{h}$$

The solution to this set of linearly dependent equations can be obtained in two ways. The first is by explicitly considering additional termination steps involving the transient free radicals. The second is by assuming that steps v and vi in Scheme I represent the only chain-terminating steps. Although these two approaches lead to slightly different kinetic expressions, the general result that the chain mechanism is [T⁻] dependent remains the same. The second method is somewhat simpler and is used here. The assumption that methyl radicals are not involved in additional chain-terminating steps to a rate-altering degree is not unreasonable in view of the difficulty of trapping methyl radical by cyclohexane or toluene under these conditions. Using this assumption, we are able to solve the set of simultaneous equations by introducing an additional equation required by the stoichiom-

(22) The error limits reported are the standard deviations for the least-squares plots. Inherent errors based upon instrumental limitations are ca. 15%.

(23) A reviewer has suggested a discrepancy between the ratio of appearance and disappearance quantum yields and reported preparative quantum yields approaching 90%. The quantum yield of appearance of triphenylethane must be increased by a factor of 31% to account for the additional product, which results in a ratio of appearance and disappearance quantum yields of 82%, within the experimental error of the quantum yield determination.

etry of the reaction (i). This allows us to eliminate $[CH_3]$ from

$$[T\cdot] = [P\cdot] + [CH_3\cdot] \tag{i}$$

eq h as follows:

$$\frac{dP\cdot^-}{dt} = k_{ra}([T\cdot] - [P\cdot])[T^-] - k_c[P\cdot] - k_{rr}[P\cdot][T\cdot] = 0 \tag{h'}$$

or

$$[P\cdot] = \frac{k_{ra}[T\cdot][T^-]}{k_{ra}[T^-] + k_c + k_{rr}[T\cdot]} \tag{j}$$

From eq e, we obtain eq k.

$$[T^{-*}] = \frac{I}{k_d + k_{et}} \tag{k}$$

Processes v and vi, being highly exothermic radical–radical or electron-transfer processes, are likely to be diffusion controlled, i.e., $k_{rr} = k'_{rr}$, so that the rate of product formation is given by eq l. Making a similar substitution for k'_{rr} and using eq e and

$$\begin{aligned}\frac{dP}{dt} &= k_c[P\cdot] + k_{rr}[P\cdot][T\cdot] + k'_{rr}[CH_3][T\cdot] \\ &= k_c[P\cdot] + k_{rr}[T\cdot]([CH_3\cdot] + [P\cdot]) \\ &= k_c[P\cdot] + k_{rr}[T\cdot]^2\end{aligned} \tag{l}$$

i in the steady-state expression (g) allows us to solve $[T\cdot]$:

$$k_{et}[T^{-*}] - k_{rr}[T\cdot]^2 = 0 \tag{g'}$$

$$[T\cdot] = \left(\frac{k_{et}[T^{-*}]}{k_{rr}}\right)^{1/2} = \left[\frac{Ik_{et}}{k_{rr}(k_d + k_{et})}\right]^{1/2} \tag{m}$$

The generalized equation for the quantum yield may be obtained by combining eq j, l, and m. However, it is most useful to consider the limiting cases so as to reduce the complexity of the expression:

A. Chain Mechanism. This mechanism implies that the chain propagation step described by k_c is not rate limiting, i.e., $k_c \gg k_{ra}[T^-]$ and $k_c[P\cdot] \gg k_{rr}[T\cdot]^2$. Thus

$$\begin{aligned}\Phi_r &= \frac{\frac{dP}{dt}}{I} = \frac{k_c[P\cdot]}{I} = \frac{k_c\left(\frac{k_{ra}[T\cdot][T^-]}{k_c}\right)}{I} \\ &= k_{ra}[T^-]\left[\frac{k_{et}}{Ik_{rr}(k_d + k_{et})}\right]^{1/2}\end{aligned} \tag{n}$$

B. Nonchain Mechanism. If $k_c \simeq 0$, the expression for the quantum yield quickly reduces to eq o.

$$\Phi_r = \frac{k_{rr}[T\cdot]^2}{I} = \frac{k_{et}}{k_d + k_{et}} \tag{o}$$

Of course, an intermediate mechanism between these two limiting cases is possible, but this does not eliminate the dependence of the quantum yield on $[T^-]$.
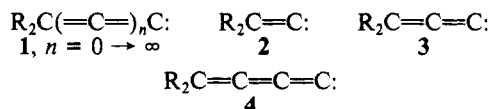
Extended Unsaturated Carbenes. Generation and Nature of Alkadienylidenecarbenes[1]

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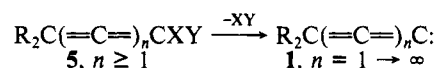
Abstract: A simple, general means of entry into alkadienylidenecarbenes, $R_2C=C=C=C:$, has been developed via base-initiated elimination of α-ethynylvinyl triflates. Trapping with tetramethylethylene results in cumulenes **10**, whereas cyclohexene gives the dimer [4]-radialenes **12**. Alkadienylidenecarbenes are definitely electrophilic with a Moss selectivity index of $m = 0.77$, and they are most likely singlets and unencumbered (not carbenoid) with little or no steric effects upon substitution.

Extended unsaturated carbenes are members of a homologous series of reactive intermediates where the electron-deficient carbenic carbon is an integral part of a π unsaturation, **1**. The

$$\underset{\substack{\mathbf{1},\,n=0\to\infty}}{R_2C(=C=)_nC:} \quad \underset{\mathbf{2}}{R_2C=C:} \quad \underset{\mathbf{3}}{R_2C=C=C:}$$
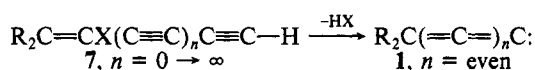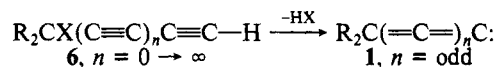
$$\underset{\mathbf{4}}{R_2C=C=C=C:}$$

first two members of the homologous series, alkylidenecarbenes **2** and alkenylidenecarbenes **3**, have been extensively investigated and their properties and chemistry widely explored.[2] In this paper we report the generation and nature of the next higher homologue (**1**, $n = 2$), the four-carbon alkadienylidenecarbene **4**.[3]

The major mode of alkylidenecarbene **2** generation is α elimination of a suitable progenitor.[2] Entry into the higher homologues, **1**, $n \geq 1$, may be gained via either α elimination of a suitably

$$\underset{\substack{\mathbf{5},\,n\geq 1}}{R_2C(=C=)_nCXY} \xrightarrow{-XY} \underset{\substack{\mathbf{1},\,n=1\to\infty}}{R_2C(=C=)_nC:}$$

functionalized cumulene **5** or via a more elaborate elimination of an appropriately functionalized polyalkyne **6** or **7**:

$$\underset{\substack{\mathbf{6},\,n=0\to\infty}}{R_2CX(C\equiv C)_nC\equiv C-H} \xrightarrow{-HX} \underset{\substack{\mathbf{1},\,n=\text{odd}}}{R_2C(=C=)_nC:}$$

$$\underset{\substack{\mathbf{7},\,n=0\to\infty}}{R_2C=CX(C\equiv C)_nC\equiv C-H} \xrightarrow{-HX} \underset{\substack{\mathbf{1},\,n=\text{even}}}{R_2C(=C=)_nC:}$$

Since cumulenes of type **5** functionalized with suitable leaving groups (halogens, tosylates, etc.) are neither known[4] nor readily accessible, we chose the more promising functionalized enynes **7** ($n = 0$) as progenitors of carbene **4**.

Results and Discussion

Generation and Trapping of Alkadienylidenecarbenes 4. Alkynylvinyl triflates **8** were prepared in good overall yields, in three

(1) Abstracted in part from the Ph.D. dissertation of T. E. Fisk, The University of Utah, 1980. Paper 13 in a series on Unsaturated Carbenes. Paper 12: Stang, P. J.; Ladika, M. *J. Am. Chem. Soc.* **1980**, *102*, 5406–07.

(2) Stang, P. J. *Chem. Rev.* **1978**, *78*, 383–405.

(3) Preliminary results were reported in a communication: Stang, P. J.; Fisk, T. E. *J. Am. Chem. Soc.* **1979**, *101*, 4772–73.

(4) For reviews on cumulenes see: *Methoden Org. Chem. (Houben-Weyl)* **1977** *5/2a*, 973–1076. Fischer, H. In "The Chemistry of Alkenes"; Patai, S., Ed.; Wiley-Interscience: London, 1964; Chapter 13, 1025–1160.