The $S_{RN}1$ Photoarylation of Indenyl Anions[1,2]

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Irradiation of Me_2SO solutions of indenyl anion and its phenylated analogues in the presence of bromobenzene produces the higher phenylated indenes. Thus indenyl anion (**1b**) yields 3-phenylindene (**3a**), 1-phenylindenyl anion (**3b**) yields 1,3- and 1,1-diphenylindene, 2-phenylindenyl anion (**2b**) produces 2,3-diphenylindene, 1,3-diphenylindenyl anion (**6b**) produces 1,1,3- and 1,2,3-triphenylindene, and 1,2-diphenylindenyl anion (**5b**) produces 1,2,3-triphenylindene (**8**). In liquid ammonia and tetrahydrofuran more complex reaction pathways are observed. The regiochemistry of phenylation is attributed to radical attack at the most basic site, in accord with a previously published model.

Introduction

The $S_{RN}1$ reaction, which provides a method for introduction of an aryl ring at a carbanionic center, continues to be a reaction of intense mechanistic and synthetic interest.[3] For the synthetic chemist the $S_{RN}1$ reaction provides a convenient and high yield method for the arylation of a carbanion via a formal nucleophilic displacement on the aryl ring, a difficult result to achieve using other methods. For the mechanistic chemist, the $S_{RN}1$ reaction provides a variety of single-electron chemistry, including electron-transfer and radical anion processes. Particularly noteworthy for both the synthetic and mechanistic chemist is the formation of a carbon–carbon bond via the reaction of a nucleophile with a radical, a new reaction in what must still be considered a rather limited set of carbon–carbon bond-forming processes. Our interest in this reaction stems mainly from our studies on the photochemistry of resonance-stabilized carbanions, which with few exceptions involves the production of radicals in the presence of carbanions and chemistry which follows the general outline of the $S_{RN}1$ process elegantly delineated by Russell[4] and Kornblum[5] and further elaborated by Bunnett.[6] One of our contributions has been the observation that, when structurally similar anions of different basicities compete, the more basic anion is also the more competitive for nucleophilic addition to the radical despite thermodynamics which favor the alternative reaction.[7] That is, the relative rate of a reaction of a radical with a resonance-stabilized carbanion is controlled not by the stability of the product radical anion, but rather by the strength of the incipient carbon–carbon bond as measured by pK_a. This generalization has been given recent independent support by Russell.[8] Thus the relative rates of reaction of certain enolates and nitronate anions can be correlated with the equilibrium acidities of the appropriate conjugate acids.

The idea that basicity controls rates of free radical addition can also be invoked to explain the regiochemistry of the $S_{RN}1$ reaction. In this case, we are dealing not with relative basicities of anions, but with relative basicities of two or more sites in an ambident anion. By an accident of nature, the free radical arylation of enolates and nitrocarbanions, which occurs at carbon rather than oxygen, yields both the most stable radical anion and the strongest bond. Generally no traces of O-arylate are found. Thus there has been little incentive to invoke a kinetic effect resulting from a thermodynamic property, basicity, to explain the observed regiochemistry when a thermodynamic effect, radical anion stability, sufficed. Norris has recently found, however, that certain sterically hindered nitrocarbanions give kinetic products involving O-alkylation,[9] suggesting that radical anion stability is not as important as previously thought. We have found that when an ambident carbanion for which the two rationales give opposite predictions is used, the product reflecting arylation at the site of highest basicity is the major one.[1]

For our preliminary studies on regioselectivity in ambident carbanions,[1] we chose the 1,3-diphenylindenyl anion. In this case, phenyl radical attack at C-1 would be preferred were site basicity to be the dominant feature. That is, since 1,3-diphenylindenyl anion is the conjugate base for *both* 1,3-diphenylindene and its less stable isomer 1,3-diphenylisoindene, simple thermodynamics require that the former be less acidic. Conversely, radical attack at C-2 would be preferred were product stability to be dominant, since the resulting 1,2,3-triphenylisoindene radical anion should be more stable than the isomeric 1,1,3-triphenylindene radical anion. In fact, C-1 attack, the kinetic process, was preferred by at least a factor of 6. A preference for C-1 rather than C-2 attack has also been observed in the photochemical $S_{RN}1$ arylation of indenyl anion itself, for which a similar rationale presumably applies. However, in the latter case experimental details are lacking.[10]

In each of these systems studied to date both formal sites of negative charge, C-1 and C-3, are equivalent by symmetry. For an unsymmetrically substituted indenyl anion—one for which C-1 and C-3 are not equivalent—additional information might be gained from the distribution of products formed from the three possible modes of attack. We therefore undertook an extension of our studies on the 1,3-diphenylindenyl anion to include all the phenylated derivatives of the indenyl anion. These studies were prompted not only by our recent work and that of Bunnett and Rossi,[10] but also by the publication by

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[1] An account of portions of this work has appeared: Tolbert, L. M.; Siddiqui, S. *Tetrahedron* **1982**, *38*, 1079.

[2] This is paper 9 of our photochemistry series. For a general review, see: Tolbert, L. M. *Org. Photochem.* **1983**, *6*, 177.

[3] (a) Wolfe, J. F.; Carver, D. R. *Org. Prep. Proced. Int.* **1978**, *10*, 225. (b) Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413. (c) Reference 15.

[4] (a) Russell, G. A.; Danen, W. C. *J. Am. Chem. Soc.* **1966**, *88*, 5663. (b) Russell, G. A.; Danen, W. C. *Ibid.* **1968**, *90*, 347.

[5] (a) Kornblum, N.; Michel, R. E.; Kerber, R. C. *J. Am. Chem. Soc.* **1966**, *88*, 5660. (b) Kornblum, N.; Michel, R. E.; Kerber, R. C. *Ibid.* **1966**, *88*, 5662. (c) Kornblum, N.; Davies, T. M.; Earl, G. W.; Holy, N. L.; Kerber, R. C.; Musser, M. T.; Snow, D. H. *Ibid.* **1967**, *89*, 725.

[6] (a) Kim, J. K.; Bunnett, J. F. *J. Am. Chem. Soc.* **1970**, *92*, 7463. (b) Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413. (c) Hoz, S.; Bunnett, J. F. *J. Am. Chem. Soc.* **1977**, *99*, 4690.

[7] Tolbert, L. M. *J. Am. Chem. Soc.* **1978**, *100*, 3952.

[8] Russell, G. A.; Mudryk, B.; Ros, F.; Jawdosiuk, M. *Tetrahedron* **1982**, *38*, 1059.

[9] Norris, R. K.; Randles, D. *J. Org. Chem.* **1982**, *47*, 1047.

[10] Rossi, R. A.; Bunnett, J. F. *J. Org. Chem.* **1973**, *38*, 3020.

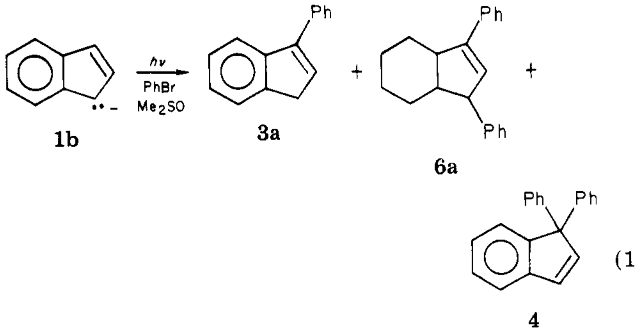
Bordwell of a detailed analysis of the equilibrium acidities of the indenes which are the subject of this study.[11] Thus we can hope to correlate the reactivities directly with the published basicities. We now report that the photophenylation of each of these derivatives exhibits regiochemistry in accord with our model. We also report new photophysical studies on 1,3-diphenylindenyl anion itself which provide new information on the photoinitiation step.

Results: Preparative Irradiations

The following indenes were obtained either commercially or by independent synthesis: indene (**1a**), 2-phenylindene (**2a**), 3-phenylindene (**3a**), 1,1-diphenylindene (**4**), 2,3-diphenylindene (**5a**), 1,3-diphenylindene (**6a**), 1,1,3-triphenylindene (**7**), and 1,2,3-triphenylindene (**8**). Solutions of the conjugate bases of indenes **1a**, **2a**, **3a**, **5a**, and **6a** were prepared in Me_2SO by deprotonation with potassium methylsulfinylmethide ("dimsyl"), in liquid ammonia by deprotonation with lithium or sodium amide, and in tetrahydrofuran with lithium diisopropylanide. The orange solutions were treated with bromobenzene, then irradiated externally using a Hanovia 450-W medium-pressure mercury arc lamp equipped with a 10^{-2} M $BiCl_3$ filter. The filter excluded all light below 350 nm and thus avoided irradiation of the neutral indenes. For relative quantum yield studies, a merry-go-round apparatus employing the identical irradiation train was used. In order to compare the photoinitiated with the dissolving metal induced arylations, the dark reactions in the presence of excess dissolving metal were also carried out. The mixtures were quenched with water, analyzed by gas chromatography, and subjected to standard isolation procedures (see Experimental Section) to identify the products.

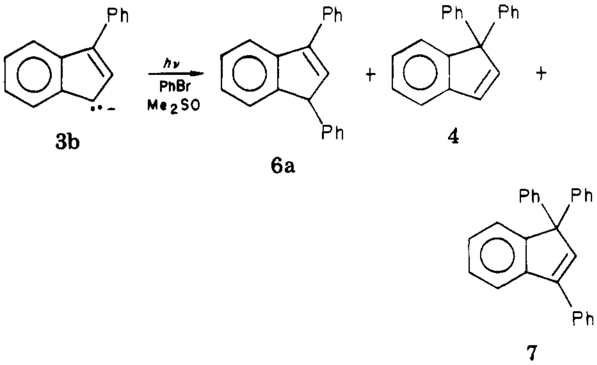
In both photoinitiated and dissolving metal induced reactions, conversions to higher arylated homologues of the indenes were observed. Particularly for the less stabilized anions, yields were modest and accompanied by dimer formation. However, reactions run to low conversion confirmed that the ratios of products observed were not artifically produced by unequal secondary reactions. The photochemical reactions could be quenched with di-*tert*-butyl nitroxide, although somewhat inefficiently. The absence of a benzyne mechanism was assured by proper choice of base concentrations and was confirmed independently.

Indenyl Anion (1b). In Me_2SO indenyl anion (**1b**) underwent facile photopromoted phenylation to yield 3-phenylindene (**3a**, 25%), as well as 1,3-diphenylindene (**6a**, 2%) and 1,1-diphenylindene (**4**, 8%). 1,1,3-Triphenylindene was also produced in 1% yield. In tetrahydrofuran, the yield of monophenyl and diphenylindenes was 30% and 8%. In this case, additional products were produced in 20% yield which apparently involved hydrogen atom abstraction. In liquid ammonia with added sodium, 3-phenylindene was produced in 35% yield, along with its reduction product 1-phenylindan. The diphenylated products were produced in 3% yield. In none of the solvents investigated was the product of 2-phenylation observed, in accord with Bunnett and Rossi's report.[10]



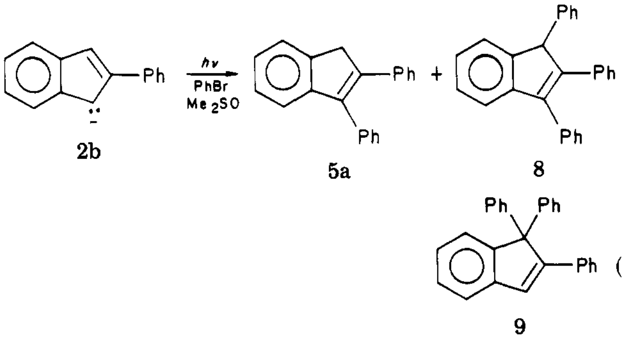
(1)

1-Phenylindenyl Anion (3b). Irradiation for 30 min of 1-phenylindenyl anion (**3b**) with bromobenzene in Me_2SO produced a 60% loss of starting material and formation of 1,1-diphenylindene (8%), 1,3-diphenylindene (2%), and 1,1,3-triphenylindene (12%) (see eq 2). No 2,3-diphenylindene could be detected. A similar experiment in liquid ammonia/potassium *tert*-butoxide produced the same indenes in ratios of 1%, 20%, and 9%, as well as 1,2,3-triphenylindene (3%) and 2,3-diphenylindene (20%). More extensive irradiation led to the disappearance of 1,1-diphenylindene from the reaction mixture.



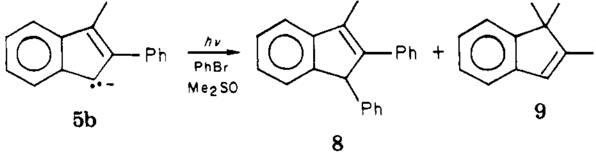
(2)

2-Phenylindenyl Anion (2b). Irradiation of 2-phenylindenyl anion (**2b**) for 80 min in Me_2SO produced 2,3-diphenylindene (**5a**, 20%) and triphenylindenes **8** and **9** (10%) (see eq 3). A 90 min irradiation in tetrahydrofuran produced the products in 17% and 32% yield. The anion did not react with bromobenzene in liquid ammonia without photostimulation. Following 60 min of irradiation in liquid ammonia, an 80% conversion of starting material was observed with the formation of 2,3-diphenylindene (**5a**, 38%) and triphenylindenes **8** and **9** (16%).



(3)

1,2-Diphenylindenyl Anion (5b). In Me_2SO containing bromobenzene both 1,2,3-triphenylindene (**8**, 20%) and 1,1,2-triphenylindene (**9**, 7%) were formed upon irradiation of this anion (see eq 4). In liquid ammonia the yields were negligible in room light and 30% of **8** and 10% of **9** after 30 min of irradiation.



(4)

1,3-Diphenylindenyl Anion (6a). The anion in Me_2SO was irradiated for 10 h with bromobenzene. The yield of 1,1,3-triphenylindene was 50%, while that of 1,2,3-tri-

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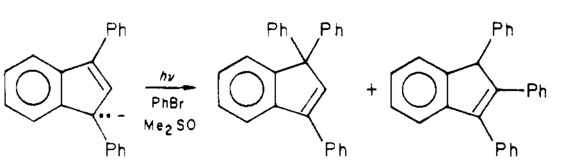
[11] Bordwell, F. G.; Drucker, G. E. *J. Org. Chem.* 1980, *45*, 3325.

phenylindene was 9% (see eq 5). More extensive irradiation reduced the yield of the 1,2,3-triphenyl isomer. Similar product ratios were observed in tetrahydrofuran, along with 28% of a solvent adduct. In liquid ammonia, the anion generated with potassium *tert*-butoxide yielded only the 1,1,3-triphenylindene. No traces of the 1,2,3-isomer could be detected. However, after 3 h of irradiation, the 1,2,3-triphenyl isomer could be detected in a 10% yield.



6b 7 8 (5)

Discussion: The Radical Anion Pathway and Its Consequences

The overall photoarylation coupled with a significant, if inefficient, quenching by di-*tert*-butyl nitroxide is consistent with the intervention of a nonchain photostimulated $S_{RN}1$ reaction, as indicated in Scheme I. Although our main concern is the regiochemistry of the key product-forming step, step f, the lack of a chain mechanism also allows us to investigate the quenching step, step c, and the photoinitiation step, step d. Finally, we investigate whether the product radical anion in step f, which does *not* rearrange upon direct formation,[1] will rearrange when formed by electron transfer from a photoexcited carbanion (eq 6).

Scheme I

(a) $\mathrm{In}^- \xrightarrow{h\nu} \mathrm{In}^{-*}$

(b) $\mathrm{In}^{-*} \xrightarrow{k_d + k_f} \mathrm{In}^-$

(c) $\mathrm{In}^{-*} + \mathrm{PhBr} \xrightarrow{k_q} \mathrm{In}^- + \mathrm{PhBr}$

(d) $\mathrm{In}^{-*} + \mathrm{PhBr} \xrightarrow{k_{et}} \mathrm{In}\cdot + \mathrm{PhBr}^{-}\cdot$

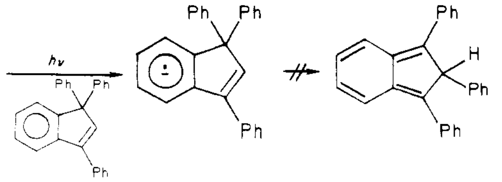
(e) $\mathrm{PhBr}^{-}\cdot \rightarrow \mathrm{Ph}\cdot + \mathrm{Br}^-$

(f) $\mathrm{Ph}\cdot + \mathrm{In}^- \rightarrow \mathrm{InPh}^{-}\cdot$

(g) $\mathrm{InPh}^{-}\cdot + \mathrm{In}\cdot \rightarrow \mathrm{InPh} + \mathrm{In}\!:^-$

(h) $\mathrm{In}\cdot + \mathrm{In}\cdot \rightarrow \mathrm{In{-}In}$

6b



(6)

The Regiochemistry of the $S_{RN}1$ Mechanism. The regioselectivity of the $S_{RN}1$ reaction has been rationalized in a variety of empirical and theoretical ways. In our previous work, we discussed the differing predictions based upon the Kornblum model,[12] which uses product stability as the driving force, and our model, which uses basicity as the criterion controlling regioselectivity. A rationale which preceded ours was presented by Rossi and is based upon a frontier orbital approach.[13,14] That is, the product arises which reflects bond formation at the atom bearing the largest orbital coefficient in the highest occupied molecular orbital (HOMO) of the carbanion. In general, the largest HOMO coefficient coincides with the site of highest charge density and basicity for a carbanion, and the two approaches are indistinguishable. However, for the case of odd-alternant hydrocarbon anions, the HOMO coefficients are often identical, and the frontier orbital approach fails. In this case, recourse must again be made to reaction control by product stability. An example is provided by the 1-phenylpropenyl anion, for which HOMO coefficients at C-1 and C-3 are identical and thus render useless a frontier orbital calculation.[14] In this case, phenyl radical attack at C-1 produces a toluene-like radical anion while attack at C-3 produces a styrene-like radical anion, and product stability favors the latter. Alternatively, if we consider the two conjugate acids of the anion, namely, 1-phenylpropene and 3-phenylpropene, simple thermodynamic considerations predict the highest pK_a for 1-phenylpropene, i.e., highest basicity at C-3. Thus our basicity argument would also rationalize the observed product without the deus ex machina of radical anion stability.

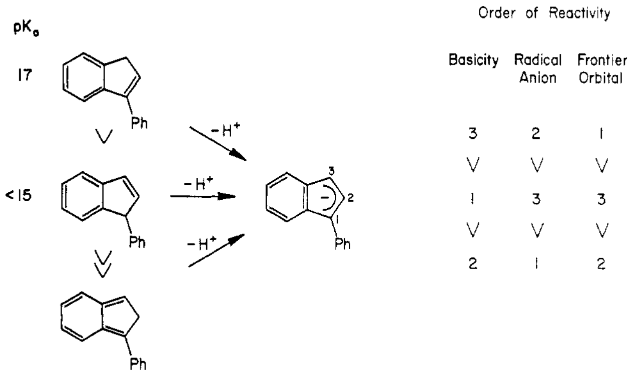


Figure 1.

The results on 1-phenylindenyl anion reported here provides a more rigorous test of these theoretical arguments, since the existence of three nonequivalent sites for radical attack allow a ready distinction among the three possibilities. We consider the three species produced by bond formation at C-1, C-2, or C-3. First, the most stable radical anion would be the isoindene produced by attack at C-2, followed by the 1,1-diphenylethylene-like moiety produced by attack at C-3. Second, a simple Hückel molecular orbital calculation yields the largest HOMO coefficient for C-1 followed by C-3, and thus predicts arylation in the order C-1, C-3, C-2. Third, consideration of the pK_a's of all three conjugate acids of anion 2b allows us to predict basicity of the three sites to follow the order C-3, C-1, and C-2. The pK_a for 3-phenylindene determined by Bordwell is 17, while that for 1-phenylindene is estimated from linear free energy considerations to be <15. Although the pK_a of the unstable 1-phenylisoindene is unknown, it is certainly several pK_a units lower than 15. Thus our basicity model predicts arylation at C-3, and then C-1. Figure 1 summarizes the predictions of each method and, of course, reiterates that the result actually observed

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[12] Kornblum, N.; Ackerman, P.; Swiger, R. T. *J. Org. Chem.* **1980**, *45*, 5294.

[13] Rossi, R. A.; deRossi, R. H. "Aromatic Substitution by the S_{RN} Mechanism"; American Chemical Society: Washington, DC, 1983.

[14] Rossi, R. A.; deRossi, R. H.; Lôpez, A. F. *J. Org. Chem.* **1976**, *41*, 3367.

corresponds to the pK_a model.

For the remaining indenyl anions, arylation in each case concides with the simple prediction based upon pK_a considerations. Thus 1,2-diphenylindenyl anion yields as the major product 1,2,3-triphenylindene, and 1,3-diphenylindenyl anion yields as the major product 1,1,3-triphenylindene. Although in principle attack at C-2 would be followed by rearrangement to give the observed products, in the case of 1,3-diphenylindenyl anion this was shown not to be a significant pathway.[1]

A caution is in order. The rule that reactions of radicals with anions are strongly influenced by the pK_a of the conjugate acid is an empirical one which can be justified through an appeal to molecular orbital correlation. That is, for exothermic reactions, an early transition state implies that the odd electron is heavily localized on the nonbonding orbital of the radical and thus its energy is insensitive to radical anion stabilization, a property of the π^* orbital of product. Since this is a transition state argument, it obviously will not be applicable in comparing reactions of grossly dissimilar nucleophiles which will have quite different transition states. The role of basicity and radical anion stability in influencing reactivity is going to be a function not only of the extent of bond formation in the transition state, but also of steric factors which may influence regiochemistry. This is dramatically illustrated by the surprising O-alkylation of sterically hindered nitrocarbanions reported by Randles and Norris.[9] Steric factors may also play a role in the contrasting regiochemistry of triphenylmethyl anion upon reaction with methyl radical or phenyl radical.[15] For this substrate, methyl radical yields mainly the product of alpha alkylation while phenyl radical yields mainly the product of para arylation.[1] Thus the regiochemistry is also sensitive to the identity of the radical, and we note that formation of the sterically less crowded products may play a role in arylation of indenyl anions as well.

Nature of the Photoiniation Step. The photoiniation step in $S_{RN}1$ reactions has been poorly understood, mainly because the typically long chain lengths obscure the identity of the initiation step. However, some light has been shed on this problem by Hoz and Bunnett,[16a] and the fact that long wavelength light apparently initiates $S_{RN}1$ reactions with nitrocarbanions suggests that charge-transfer complexes may be important.[16b] In the case of the indenyl anions, the lack of a free-radical chain simplifies the kinetics and makes possible determination of the initiation step for these species.

Since the use of filter solutions rigorously excludes absorption of light by species other than the carbanion and its possible complexes, the salient feature of the photoiniation concerns the mechanism of the electron transfer from photoexcited anion to bromobenzene. If this process is truly collisional, as steps c and d of Scheme I imply, then fluorescence quenching and product formation will exhibit classical Stern–Volmer sensitization kinetics, eq 7 and 8.

$$\frac{\Phi_0}{\Phi_f} = 1 + \frac{(k_{et} + k_q)[Q]}{k_d + k_f} = k_q'\tau[Q] \tag{7}$$

$$\frac{\Phi_\infty}{\Phi_r} = 1 + \frac{k_d + k_f}{k_{et} + k_q}[PhBr]^{-1} \tag{8}$$

Moreover, determination of the excited state lifetime of the anion should allow us to determine k_q' (= $k_q + k_{et}$) for the quenching process and thus to ascertain if the electron-transfer process is collisional.

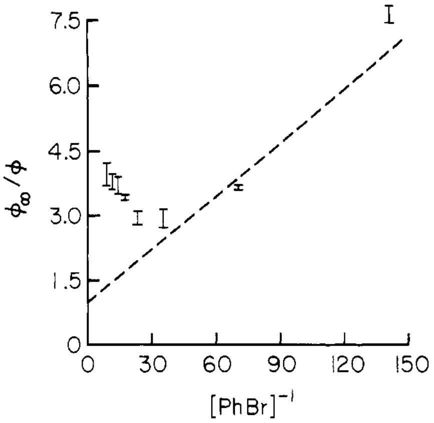

Figure 2.

Table I. Quenching Studies

acceptor	$k_q'\tau$, L mol^{-1}	k_q, L mol^{-1} s^{-1} × 10^{-9}
PhCl	20.8 ± 0.6	1.89 ± 0.05
PhBr	33.1 ± 4.4	3.01 ± 0.40
PhI	51.2 ± 1.4	4.65 ± 0.13
Ph_2	46.2 ± 0.2	4.20 ± 0.02
$C_{10}H_8$	61.6 ± 2.0	5.60 ± 0.18

Results

Electron-Transfer Quenching of 1,3-Diphenylindenyl Anion Photoreactivity. The clean reaction of 1,3-diphenylindenyl anion, as well as its strong fluorescence, made this anion ideal for exploring the initiation step. Furthermore, the similarity of its absorption and emission spectra with those of the isoelectronic 1,3-diphenylisobenzofuran provided a convenient standard for determination of its fluorescence quantum yield. For fluorescence quenchers, we chose aromatic hydrocarbons biphenyl and naphthalene, i.e., aromatic hydrocarbons with $E_{1/2} < -2.2$ V, which would readily undergo reduction by the carbanionic excited state but for which energy transfer would be endoergic. We also included bromobenzene, chlorobenzene, and iodobenzene, i.e., typical substrates for the $S_{RN}1$ reaction.

From a relative quantum yield of 0.72 and the reported fluorescence quantum yield for 1,3-diphenylisobenzofuran of 0.96,[17] we calculated a corrected fluorescence quantum yield of 0.69. The fluorescence quenching of 1,3-diphenylindenyl anion was also measured by using standard additions of the aromatic hydrocarbons and halocarbons. A plot of relative quantum yield vs. quencher concentration (eq 7) yielded linear plots with slopes ($k_q'\tau$) slightly dependent upon the identity of quencher (see Table I). The excited state lifetime determined by single-photon counting was 11 ns, thus permitting calculation of the quenching rate constants, also entered in Table I.

The relative yield of triphenylindenes from phenylation of 1,3-diphenylindenyl anion in Me_2SO containing bromobenzene was found to depend inversely upon bromobenzene concentration at the lower values, in accord with eq 8 (see Figure 2). A least-squares treatment of the relative quantum yield of the three lowest concentrations (six data points) yielded a slope of 0.045 ± 0.020 mol L^{-1}, i.e., $k_q'\tau$ 22 ± 10 L mol^{-1}. At higher concentrations, however, the quantum yield actually decreased with increasing bromobenzene.

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[15] Tolbert, L. M.; Martone, D. P. *J. Org. Chem.* **1983**, *48*, 1185.

[16] (a) Hoz, S.; Bunnett, J. F. *J. Am. Chem. Soc.* **1977**, *99*, 4690. (b) Wade, P. A. Ph.D. Thesis, Purdue University, 1973. (c) See also Fox, M. A.; Younathan, J.; Fryxell, G. E. *J. Org. Chem.* **1983**, *48*, 3109.

[17] Olmsted III, J.; Akasha, T. *J. Am. Chem. Soc.* **1973**, *95*, 6211.

Attempted Electron-Transfer Induced Phenyl Migration of Di- and Triphenylindenes. We have observed that irradiation of triphenylmethyl anion in the presence of *cis*-stilbene induces facile cis–trans isomerization via an electron-transfer pathway.[18] Since 1,2,3-triphenylindene is apparently a secondary product of the arylation in liquid ammonia of 1,3-diphenylindene, we investigated the possibility of a photochemically promoted electron-transfer induced rearrangement of 1,1,3-triphenylindene via the mechanism reported by Miller.[19] Neither irradiation of triphenylmethyl anion in Me_2SO nor irradiation of 1,3-diphenylindenyl anion in liquid ammonia with 1,1,3-triphenylindene as the electron acceptor at concentrations which quench the anion fluorescence produced detectible amounts of the rearranged product (see eq 6). A similar irradiation of 1,3-diphenylindenyl anion in the presence of 1,1-diphenylindene in Me_2SO failed to produce the radical anion rearrangement product 1,2-diphenylindene. This result supports Kiesele's contention that such rearrangements involve dianions rather than radical anions.[20]

Discussion

Nature of the Carbanionic Excited State and the Initial Electron-Transfer Event. Using the Debye–Hückel equation, the diffusion-controlled rate constant at 25 °C in Me_2SO is 3.2×10^9 L mol^{-1} s^{-1}, assuming a viscosity at that temperature of 1.99 cP.[21] Fluorescence-quenching rate constants for several quenchers in Table I are greater than the diffusion-controlled limit. For the lower indenyl anions, e.g., **2b**, color changes were observed upon addition of bromobenzene which could be attributed to ground-state complexes. The presence of larger-than-diffusion-controlled quenching rates could reflect the involvement of ground-state complexes for 1,3-diphenylindenyl anion as well. However, the shape of the fluorescence and excitation spectra, as well as the absorption spectra, were unaffected by the addition of electron-transfer quenchers. Thus we conclude that ground-state complexes are not involved in the photophysics of this anion at these concentrations. It is attractive to consider the possibility that these higher rates reflect the larger cross section of the carbanionic state. Given the errors associated with such measurements, however, the most defensible conclusion is that electron transfer occurs at the diffusion-controlled rate. Significantly, the ordering and relative magnitude of differences among the various electron acceptors is quite similar to those obtained by Bunnett for aryl halides in the $S_{RN}1$ reaction, in which the electron donor is not an excited state but rather the radical anion of a ketone.[22] Thus we conclude that the photochemical electron-transfer step is mechanistically equivalent to the ground-state electron transfer and may bear upon the π^* vs. σ^* nature of the aryl halide radical anion. For the carbanionic excited states, the electron transfer is clearly exoergonic, and the rates of electron transfer in that region, as predicted by current theory, are near diffusion limits. The minor variation among various acceptors may be due to one of several factors. In addition to the possibility of involvements of π^* radical anion states, this variation also correlates somewhat with the size of the acceptor, in accord with the Stokes–Einstein theory.[23]

Although these results are permissive for the involvement of a collisional electron transfer in the product forming sequence, the inverse quantum yield dependence upon bromobenzene concentration of Figure 2 is more compelling. Thus the values of $k_q'\tau$ determined both by fluorescence quenching and relative quantum yield determination are within experimental uncertainty. To our knowledge this is the first experimental confirmation of the mechanism of the photoinitiation step in an $S_{RN}1$ reaction.

The paradoxical decrease in quantum yield at higher bromobenzene centrations may be due to two or more factors. One possibility is the formation of ground-state charge-transfer complexes which are less efficient at promoting the reaction. Another possibility is that, at high bromobenzene concentration, the electron transfer occurs within a solvent cage, leading to rapid back-electron transfer and quenching. The latter possibility is strengthened by the observation that nonlinearities were observed only for product formation and not for fluorescence quenching. That is, ground-state charge-transfer complexes should have been observed both as nonlinearities in the Stern–Volmer fluorescence quenching plots and as nonlinear effects on the excitation spectra. None of these was observed.

Conclusions

The photoarylation of indenyl anions is characterized by an initial collisional electron-transfer step from the carbanion excited state. The phenyl radical resulting from electron transfer to aryl halide adds to the indenyl anion at the most basic site. Thus basicity provides a convenient predictive tool in $S_{RN}1$ chemistry which, as all generalizations, must be used with caution among substrates of dissimilar structure. The regiochemistry is also sensitive to the identity of the radical, and we note that formation of the sterically less crowded products may play a role in arylation of indenyl anions as well.

Experimental Section

Materials. Indene (Aldrich) was distilled prior to use. 3-Phenylindene (**3a**) was prepared by dehydration of 1-phenyl-1-indanol prepared from phenylmagnesium bromide and indanone.[11] 2-Phenylindene (**2a**), mp 174–175 °C (lit.[27] mp 167.5 °C) was synthesized using the procedure of Braun and Manz.[24] 2,3-Diphenylindene (**5a**), mp 112–113 °C (lit.[26] mp 108 °C), was obtained by Bordwell's procedure.[11] 1,1-Diphenylindene (**4**) was synthesized following the procedure of Miller and Boyer.[27] The yield of colorless crystals, mp 85–86 °C (lit.[27] mp 91–92 °C), was 74%. The melting point did not increase upon recrystallization and was analytically pure. 1,3-Diphenylindene (**6a**) was synthesized by pyrolysis of the magnesium salt of 1,1,3-triphenyl-2-propen-1-ol.[28] 1,1,3-Triphenylindene (**7**) was synthesized by the method of Hodgkins and Hughes[29] and had mp 132–133 °C (lit.[29] mp 135–136 °C). 1,2,3-Triphenylindene (**8**) was generated most conveniently by preparative irradiation of 1,1,3-triphenylindene using a Pyrex-filtered 450-W medium-pressure mercury arc lamp. The yield of rearranged indene, mp 130–131 °C (lit.[30] mp 130–132 °C), was 80%.

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Solvents. Me_2SO was purified using Bordwell's procedure.[31] Tetrahydrofuran was freshly distilled from sodium benzophenone ketyl in a deoxygenated argon atmosphere. Liquid ammonia was doubly distilled. All manipulations were carried out in an atmosphere of argon which had been purified using an Ace-Burlitch inert atmosphere system.

General Procedure for Irradiation of Indenyl Anions. A. In Me_2SO. To a 35-mL irradiation tube equipped with a detachable 4-mm three-way stopcock and an external water jacket, 0.1 to 1 mmol of hydrocarbon was added. The tube was degassed by evacuating and purging three times with argon. Freshly distilled dimethyl sulfoxide was added to the degassed apparatus containing the indene (0.01–0.02 M) by reaching through the bore of the three-way stopcock with the needle of a degassed syringe while a constant stream of argon was maintained through the side opening of the stopcock. The potassium salt of the indenyl anion was generated by adding a freshly prepared solution of potassium *tert*-butoxide in dimethyl sulfoxide in 5–20% excess. The solution was allowed to equilibrate for 30 min at room temperature. After addition of 1–2 equiv of halobenzene from a freshly opened bottle, the colored anion was irradiated using the appropriate filter. Irradiation of the anion was monitored by gas chromatography to about 50–70% conversion (30 min to 10 h). The reaction mixture was quenched with 1% hydrochloric acid and the products were analyzed by gas chromatography by adding a known amount of internal standard. For a sample preparative run of each indene, the quenched reaction mixture was extracted several times with dichloromethane. The combined organic extracts were washed three times with a brine solution and finally dried over anhyd $MgSO_4$. After removal of solvent in vacuo the residue was chromatographed on a 2.0 × 75 cm silica gel column using ether–hexane as eluent. The products were characterized by their melting points, infrared and mass spectra, as well as NMR and carbon and hydrogen analysis for new compounds. The percentages of the isolated products reported are based on recovered starting material.

B. In Tetrahydrofuran (THF). The indenyl anion was prepared by treatment of 1 mmol of the appropriate indene in 50 mL of dry THF with 1 mmol of freshly prepared lithium diisopropylamide (LDA) at 0 °C followed by equilibration for 30 min at room temperature. Bromobenzene (0.2 mL, 2 mmol) was added, the solution was irradiated for 6–8 h and quenched with dilute (1%) HCl, the solvent was removed *in vacuo*, and the residue was taken up in an ether–water mixture. The solution was washed with dilute HCl. The ether fraction was dried over anhydrous magnesium sulfate and concentrated in vacuo. The products were analyzed by preparative thin-layer or column silica gel chromatography.

C. In Liquid Ammonia. A 15–20 mL volume of anhydrous ammonia was condensed into a 100-mL vacuum-jacketed irradiation vessel equipped with a Dewar condenser containing dry ice/acetone. A 1-mmol portion of freshly cut sodium metal was added to the stirred ammonia, followed by one or two small crystals of hydrated ferric nitrate. After amide formation was complete, an ethereal solution containing 1 mmol of indene was added. The anion was allowed to equilibrate for 30 min and 1 mmol of halobenzene in 1–2 mL of ether was added. The reaction mixture was irradiated under positive argon pressure using an appropriate optical filter for 30 min to 3 h. The reaction was quenched by adding solid NH_4Cl, and the ammonia was allowed to evaporate. The reaction mixture was taken up in ether, and the solid was removed by filtration and then washed with ether. A weighed amount of an internal standard was added to the combined ethereal extracts and the products were analyzed by comparison with a standard mixture. Isolation of products was achieved by silica gel (Grace Grade 62) column chromatography. The products were characterized by nuclear magnetic resonance, mass spectroscopy, and in the case of new compounds, elemental analysis. In some cases, potassium *tert*-butoxide or lithium amide were used as bases. For potassium *tert*-butoxide, the solid material was placed in the reaction flask and degassed several times prior to addition of liquid ammonia. For lithium amide, 0.5 mL of 1.6 M *n*-butyllithium in hexane (0.8 mmol) was added to the liquid ammonia. Otherwise the procedure described above was used.

Dark Reactions of Indenyl Anions with Halobenzene in the Presence of Solvated Electrons. The procedure was similar to that described above for photochemical reactions in liquid ammonia up to the addition of halobenzene. This was followed by addition of excess sodium. The reaction mixture was quenched and analyzed as above.

Irradiation of Indenyl Anion (1b). A. Potassium Salt in Me_2SO. An 8-mL Me_2SO solution containing 224 mg (2 mmol) of potassium *tert*-butoxide was added to 186 mg (1.6 mmol) of freshly distilled indene in 25 mL of Me_2SO. After equilibration of the light yellow anion, 160 mg (1 mmol) of bromobenzene was added whereupon the solution became light red. (An aliquot (1 mL) was quenched with water and analyzed by gas chromatography.) The anion solution was irradiated for a total of 30 min when the solution became dark red. The reaction mixture was quenched and analyzed by gas chromatography using biphenyl as the internal standard. 3-Phenylindene (15%) was the major product. Other products identified were 1,1- and 1,3-diphenylindene (<10%) and 1,1,3-triphenylindene (1%).

B. Lithium Salt in Tetrahydrofuran. To 246 mg (2.13 mmol) of distilled indene in 50 mL of dry THF was added 12 mL of freshly prepared THF solution of 0.16 M (1.92 mmol) lithium diisopropylamide (LDA) at 0 °C. After equilibration of the yellow anion, 303 mg (0.2 mL, 1.92 mmol) of bromobenzene was added to the above solution upon which the solution became deep red. The reaction was stirred in the room light for 30 min and quenched. The products were quantitated by adding an etheral solution of biphenyl (32 mg) to the reaction mixture in ether (after extraction). The products were 3-phenylindene (30%), 1,1- and 1,3-diphenylindene (8% combined yield), and an intractable residue (20%).

In a similar experiment, the products were isolated by silica gel column chromatography using hexane as solvent. 3-Phenylindene was isolated in 20% yield. Both 1,1- and 1,3-diphenylindene were formed in total 5% yield.

In a separate experiment using the same general procedure as described above, the indenyl anion in the presence of 50% excess bromobenzene was irradiated for 1 h with the 0.01 M $BiCl_3$ filter. Analysis by GC revealed a substantial decrease in the yield of 3-phenylindene (10%) and 1,3-diphenylindene (1%) with the appearance of the products 1,1,3-triphenylindene (10%) and 1,2,3-triphenylindene (2%).

C. Lithium Salt in Liquid Ammonia (Unirradiated). A 186-mg (1.6 mmol) portion of distilled indend in 2 mL of anhydrous ether was added to 1.6 mmol of lithium amide in 20 mL of liquid ammonia. The yellow anion solution was stirred for 30 min and 250 mg (approx. 1.6 mmol) of bromobenzene in 1 mL ether was added and the reaction mixture was stirred for 25 min in the room light and quenched by adding solid ammonium chloride. The reaction mixture was extracted with ether after removal of ammonia. A known amount (30 mg) of biphenyl was added to the ethereal solution of the mixture to quantitate unreacted indene and products against calibrated known mixtures. The major product was 3-phenylindene (35%). Other products identified were 1,1- and 1,3-diphenylindenes, in 2–3% overall yield. The mass spectra of the crude isolated mixture revealed formation of the reduction product 1-phenylindan to some extent (4% by GC). 3-Phenylindene was isolated by silica gel thin-layer chromatography using hexane and characterized by NMR and MS (isolated yield, 20%).

Irradiation of 1-Phenylindenyl Anion (3b). A. Potassium Salt in Me_2SO. A 1.5-mL solution of 0.1 M potassium *tert*-butoxide in Me_2SO was added to 27 mg (0.14 mmol) of 1-phenylindene in 6.0 mL of Me_2SO. After equilibration of the yellow anion, 15 μL (0.14 mmol) of bromobenzene was added. An aliquot (0.2 mL) quenched with water prior to irradiation showed no product formation (<0.1%) by gas chromatography. The reaction mixture was irradiated for 50 min using the 0.01 M $BiCl_3$ solution, and then analyzed by gas chromatography using triphenylmethane and triphenylethylene as internal standards. The composition of the reaction mixture was as follows: 1,1-diphenylindene (8%), 1,3-diphenylindene (2%), and 1,1,3-triphenylindene (12%). When the above reaction was performed

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using 2 equiv of bromobenzene, the product ratios remained unchanged.

B. Sodium Salt in Liquid Ammonia (Dark Reaction). The anion was generated from 23.0 mg (0.12 mmol) of 1-phenylindene and 0.12 mmol of sodium amide in 10–12 mL of ammonia in the usual way. Bromobenzene (2.0 mg, 0.15 mmol) in 1 mL of ether was added. Sodium metal (2.8 mg, 0.12 mmol) was added to the solution and the reaction mixture was quenched with solid ammonium chloride. Gas chromatographic analysis of the ethereal solution containing the mixture revealed product formation to an extent of 1%. 1-Phenylindan was formed in 10% yield.

C. Sodium Salt in Liquid Ammonia. A solution of 40 mg (0.2 mmol) of 1-phenylindene in 1.5 mL of ether was added to the freshly prepared sodium amide (0.2 mmol) in 15–20 mL of ammonia. After equilibration, 30 mg (0.2 mmol) of bromobenzene in 0.5 mL of ether was added. The reaction mixture was irradiated for 30 min by using the 0.01 M BiCl$_3$ filter. Gas chromatographic analysis of the reaction mixture in ether showed formation of 1,3- and 2,3-diphenylindene in an overall 15% yield. 1,1,3-Triphenylindene was formed in 5% yield. A trace amount of 1,1-diphenylindene (0.5%) could be detected by the analysis.

D. Potassium Salt in Liquid Ammonia. 1-Phenylindene (40 mg, 0.20 mmol) in 1 mL of anhydrous ether was added to a stirred suspension of 25 mg (0.2 mmol) of potassium *tert*-butoxide in 15–20 mL of liquid ammonia under an atmosphere of argon. Bromobenzene (60 mg, 0.4 mmol) in 0.5 mL of ether was added to the yellow solution and the reaction mixture irradiated for a total of 30 min by using the 0.01 M BiCl$_3$ filter. The solution became orange-red. Triphenylethylene (10 mg) was added as internal standard, and the solution was analyzed by gas chromatography; 1,3- and 2,3-diphenylindenes were produced in a combined yield of 40%. 1,1,3-Triphenylindene was produced in 9% and 1,2,3-triphenylindene in 3% yield. 1,1-Diphenylindene was achieved in 1% yield. When the same reaction in a separate experiment was irradiated for 90 min, the yield of combined 1,3- and 2,3-diphenylindene was 26%, 1,1,3-triphenylindene was 10%, and 1,2,3-triphenylindene was produced in 10%. No 1,1-diphenylindene was detected in the reaction mixture.

Irradiation of 2-Phenylindenyl Anion (2b). A. Potassium Salt in Me$_2$SO. A 30-mL dimethyl sulfoxide solution of the greenish yellow conjugate base of 2-phenylindene from 58 mg (0.3 mmol) of 2-phenylindene and potassium *tert*-butoxide (30% molar excess) was irradiated in the presence of 47.1 mg (0.3 mmol) of bromobenzene using a 0.01 M BiCl$_3$ filter for a total time of 80 min. Gas chromatographic analysis of the quenched mixture using triphenylethylene revealed formation of 2,3-diphenylindene (20%) and 1,2,3- and 1,1,2-triphenylindenes (10%) in a ratio of 2:1.

B. Potassium Salt in Me$_2$SO with Iodobenzene. Solutions of 0.02 M 2-phenylindenyl anion were generated from equimolar amounts (0.104 mmol) of 2-phenylindene, 1 mL of 0.12 M potassium *tert*-butoxide in Me$_2$SO, and 4 mL of Me$_2$SO in two 15-mL irradiation tubes marked 1 and 2. To tubes 1 and 2 were added 21.6 mg (0.104 mmol) and 44 mg (0.21 mmol) of iodobenzene respectively whereupon the yellow solutions became red. After 30 min at room temperature, an aliquot (100 μL) was withdrawn from each tube and the reaction mixture analyzed by gas chromatography. Each tube showed formation of products 2,3-diphenylindene and 1,2,3-triphenylindene to an extent of overall 2% yield. Two tubes containing the above solutions were placed on a merry-go-round so as to ensure uniform light capture and were irradiated using a 0.01 M BiCl$_3$ filter solution for a total of 90 min. The quenched reaction mixtures were quantitated against triphenylethylene as the internal standard. Tube 1 had 2,3-diphenylindene (20%) and 1,2,3-triphenylindene (4%), tube 2 had 20 and 2% of the same products, respectively.

C. Lithium Salt in Tetrahydrofuran. To 57 mg (0.3 mmol) of 2-phenylindene in 10 mL of dry THF was added 0.3 mmol of freshly prepared lithium diisopropyl amide in 10 mL of THF at 0 °C. To the equilibrated solution was added 50 mg (0.3 mmol) of bromobenzene at room temperature. The reaction mixture was irradiated 1.5 h and quenched. Gas chromatographic analysis of the mixture using triphenylethylene as the internal standard gave the following: 2,3-diphenylindene (17%) and 1,2,3-triphenylindene (32%). Other products were unidentified.

D. Sodium Salt in Liquid Ammonia (Dark Reaction). To the equilibrated anion made from 29.2 mg (0.15 mmol) of the 2-phenylindene and an equivalent of sodium amide in 12–15 mL of liquid ammonia was added an ether solution of 24 mg (0.15 mmol) of bromobenzene. Sodium (3 mg) was added and the solution stirred in the room light for 30 min. The reaction was quenched and the ethereal extract of the mixture showed 2–3% diphenylindene by gas chromatography. No 1,2,3-triphenylindene was detected by GC. GC traces also showed formation of 2-phenylindan to a 20% extent.

E. Sodium Salt in Liquid Ammonia. To the stirred green-yellow anion of 2-phenylindene generated as above was added an ethereal solution of 0.15 mmol bromobenzene. The reaction was irradiated for 60 min by using a 0.01 M BiCl$_3$ filter. 1,1,2,2-Tetraphenylethane (4.2 mg) was added to the extract of the quenched reaction mixture and the products were analyzed by gas chromatography. The yield of 2,3-diphenylindene was 38% and that of 1,2,3-triphenylindene was 16%.

Irradiation of 1,2-Diphenylindenyl Anion (5b). A. Potassium Salt in Me$_2$SO. The green solution of 2,3-diphenylindenyl anion, from 80 mg (0.3 mmol) of the hydrocarbon in 11 mL of Me$_2$SO and 3 mL of a 0.11 M Me$_2$SO solution of potassium *tert*-butoxide (0.33 mmol), was irradiated in the presence of 0.3 mmol of bromobenzene by using a 0.01 M BiCl$_3$ filter solution. The reaction mixture, which at the end of 4 h had become deep red, was quenched with water. Triphenylethylene was added as an internal standard and gas chromatographic analysis of the mixture showed 1,2,3-triphenylindene (20%) as the major product. 1,1,2-Triphenylindene was formed in 7% yield. Further irradiation of a similar reaction mixture up to 5 h resulted in a 17% yield of 1,2,3-triphenylindene and an 8% yield of 1,1,2-triphenylindene, as analyzed by gas chromatography and NMR.

B. Sodium Salt in Liquid Ammonia (Dark Reaction). To the freshly prepared 0.11 mmol of sodium amide in 12–15 mL of ammonia was added 1 mL of ethereal solution containing 31 mg (0.115 mmol) of 2,3-diphenylindene. A 19-mg (0.12 mmol) portion of bromobenzene in ether was added to the anion in ammonia followed by 2 mg of sodium. The reaction was stirred for 30 min in the room light and quenched. Gas chromatography showed the presence of 1,2,3-triphenylindene (trace) and 1,2,3-triphenylindan in 2% overall yield.

C. Sodium Salt in Liquid Ammonia. The green-yellow anion was generated from 2.95 mg (0.11 mmol) of 2,3-diphenylindene and an equilvalent amount of sodium amide in 12–15 mL of ammonia. A 30-mg (0.2 mmol) portion of bromobenzene in ether was added and the reaction mixture irradiated for 30 min by using a 0.01 M BiCl$_3$ filter. Triphenylethylene (5.5 mg) was added to the ethereal extract of the reaction mixture and the products were analyzed by gas chromatography. The mixture contained 1,2,3-triphenylindene (30%), 1,2,3-triphenylindan (3%), and 1,1,2-triphenylindene (10%).

A repeat experiment with 90 min irradiation yielded 1,2,3-triphenylindene (23%), 1,2,3-triphenylindan (4%), and 1,1,2-triphenylindene (10–12%).

Irradiation of 1,3-Diphenylindenyl Anion (6b). A. With Added 1,1,3-Triphenylindene in Me$_2$SO. The anion was made from 1,3-diphenylindene (27 gm, 0.1 mmol), 1.0 mL of 0.10 M potassium *tert*-butoxide in Me$_2$SO, and 3.0 mL of Me$_2$SO in a 15-mL photolyzing tube. After equilibration of the anion (30 min), 1,1,3-triphenylindene (6 mg, 0.02 mmol) in 2.0 mL of dimethyl sulfoxide was added to the tube. The solution was irradiated for 10 h by using a K$_2$CrO$_4$ filter solution. Gas chromatographic analysis of the quenched reaction mixture showed no detectable amount of 1,2,3-triphenylindene.

B. With Added 1,1,3-Triphenylindene in Liquid Ammonia. The anion of 1,3-diphenylindene was generated from 40 mg (0.15 mmol) of the hydrocarbon, 17 mg (0.15 mmol) of potassium *tert*-butoxide, and 18–20 mL of ammonia. To the stirred solution was added 5 mg (0.015 mmol) of 1,1,3-triphenylindene in ether and the reaction mixture irradiated for 3 h with a 0.01 M BiCl$_3$ filter. Gas chromatographic analysis of the quenched reaction mixture showed no 1,2,3-triphenylindene within the limits of the GC detection system (<0.1%).

C. Comparative Irradiation with Bromo- and Iodobenzene in Me$_2$SO. Tube 1 containing 26.8 mg (0.1 mmol) of 1,3-diphenylindene in 4 mL of dimethyl sulfoxide, 1 mL of 0.1 M potassium *tert*-butoxide in dimethyl sulfoxide, and 63 mg (0.4 mmol) of bromobenzene and tube 2 containing the same anion

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in the same molar concentration but having 82 mg (0.4 mmol) of iodobenzene were irradiated on a merry-go-round apparatus. The irradiation was stopped at the end of 1 h and an aliquot (0.1 mL) was analyzed after quenching by gas chromatography. Tube 1 showed 20% of the amount of product produced in tube 2 containing iodobenzene. Irradiation was carried for a total of 6 h and the reaction mixtures were quenched with equal amounts of water (1 mL). Triphenylethylene in 2 mL of tetrahydrofuran was added to each tube and the products were quantitated. Tube 2 showed 49% of 1,1,3-triphenylindene and 8.5% of 1,2,3-triphenylindene compared to 11% and 1.7% of the respective products produced in tube 1.

Emission Studies. Purification of Solvent. Dimethyl sulfoxide was purified by the procedure of Bordwell and coworkers.[31] Benzene was purified by repeated washings with cold, concentrated sulfuric acid until the washings were colorless, then with water, and 5% sodium hydroxide, drying over anhydrous potassium carbonate, and distillation.

Fluorescence Quenching Studies. An Aminco-Bowman spectrofluorimeter equipped with a xenon lamp was used to obtain relative quantum yields for 1,3-diphenylindenyl anion in dimethyl sulfoxide. Absorption spectra were recorded on a Beckman-Model 26 spectrometer. 1,3-Diphenylindenyl anion has absorption maxima at 444 nm (ϵ 27000) and 396 nm (ϵ 19500) and an emission maximum at 476 nm. For the quenching experiments, solutions of 1,3-diphenylindenyl anion in 10 mL of Me_2SO were prepared by using a measured amount of the hydrocarbon to obtain an absorbance of 1.0 (concentration of the anion was approximately 4.0×10^{-5} M) in a 50-mL cylindrical Pyrex tube equipped with a three-way stopcock and a 1-cm cuvette at the bottom. Concentrated solutions of quencher in dimethyl sulfoxide were prepared so that the addition of 0.1 mL of quencher solution was sufficient to produce measurable quenching. The fluorescence spectrum was obtained after each of five serial additions of quencher, each being traced at least three times, the areas determined by planimetry, and the best slope of the relative quantum yield vs. quencher concentration determined by the least-squares technique. The relative quenching rates ($k_q\tau$) obtained are listed in Table I.

Fluorescence Quantum Yield (ϕ_f) of 1,3-Diphenylindenyl Anion. The quantum yield of fluorescence of 1,3-diphenylindenyl anion was measured relative to the known quantum yield of 0.96 for 1,3-diphenylisobenzofuran chosen as the standard. 1,3-Diphenylisobenzofuran was selected as the standard because of the close similarity between its absorption and emission (λ_{max} 424 nm, λ_{em} 480 nm) and those of 1,3-diphenylindenyl anion (λ_{max} 444 nm, λ_{em} 476 nm). 1,3-Diphenylindenyl anion in dimethyl sulfoxide and 1,3-diphenylisobenzofuran in deoxygenated benzene were made in two separate 50-mL cylindrical Pyrex tubes equipped with a three-way stopcock and a 1-cm cuvette at the bottom. Concentrations were adjusted so as to have almost equal absorbances for the solutions. The solutions were then maintained under an atmosphere of argon. The method of optical dilution was employed, using the following equation:[32]

$$\phi_x = \phi_r(D_x/D_r)\ (n_x^2/n_r^2)$$

where ϕ_x is the fluorescence quantum yield, D is the integrated area under the emission spectrum, n is the refractive index of the solution and, x and r refer to the unknown and reference solutions, respectively. The emission spectra were recorded on an Aminco-Bowman spectrofluorimeter and absorption spectra on a Beckman-Model 26 UV-vis spectrophotometer. The ϕ_f of 1,3-diphenylindenyl anion thus obtained was 0.69 ± 0.03 (an average of 4 separate runs). This value remained reproducible over the excitation range of 400-430 nm.

Lifetime Measurements. The fluorescence lifetime of 1,3-diphenylindenyl anion was determined by single photon counting using a Photochemical Research Associates nanosecond fluorimeter. A lamp flash of 1.6 ns width at half height allowed direct determination of excited-state decay rates by least-squares analysis of the last 350 of 512 channels, ignoring the initial channels involving the excitation region. The lifetime was determined to be 11.0 ns.

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Homolytic Displacement at Saturated Carbon. 9. The Reactions of Trichloromethanesulfonyl Chloride with Pent-4-enylcobaloximes and with Olefins. A Novel Route to (Trichloroethyl)sulfolanes via an $S_{H}i$ Mechanism

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Pent-4-enylcobaloximes react with trichloromethanesulfonyl chloride in inert solvents under irradiation with tungsten lamps to give good yields of 2-(β,β,β-trichloroethyl)sulfolanes. The same products are formed in the thermal reactions in the presence of an excess of sulfur dioxide. Studies of the reactions of related olefins with trichloromethanesulfonyl chloride catalyzed by the photolysis of secondary organocobaloximes under mild conditions show that substituted 3,3,3-trichloropropyl radicals are capable of capturing sulfur dioxide. This allows us to account for the formation of the sulfolanes by a mechanism which includes a homolytic displacement of cobaloxime(II) from saturated carbon. The latter is confirmed by the observation that the isomers of 2-methyl-5-(β,β,β-trichloroethyl)sulfolane formed from (*R*)-hex-5-en-2-ylcobaloxime are in substantial enantiomeric excess. 3-Chloro-1,1-dioxothiacyclohexanes formed as minor products indicate that pent-4-ene-1-sulfonyl radicals cyclize to 1,1-dioxothiacyclohex-3-yl radicals rather than to the corresponding five-membered sulfolanylmethyl radicals.

We recently described[1] some non-chain free radical reactions of alkylcobaloximes with trichloromethanesulfonyl chloride in which alkyl radicals, formed by photolysis of the carbon-cobalt bond, reacted with sulfur dioxide to give

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