Carbanion Photochemistry. 8. Effect of Substituent Reduction Potential on the Ground- and Excited-State Isomerization of 2-Aryl-1,3-diphenylpropenyl Anions

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The ground- and excited-state chemistry of 2-aryl-1,3-diphenylpropenyl anions is readily described by a Hückel model. Because of the antisymmetric nonbonding molecular orbital, in the ground state none of the charge is distributed in the central ring. In the excited state, a nonbonding electron is promoted to a symmetric orbital which is localized on the central aryl ring. Thus lowering the reduction potential of the substituent stabilizes the excited state toward electron-transfer-initiated isomerization of *cis*-stilbene. Conversely, the more stabilized excited states undergo more efficient *E,Z* isomerization. Finally, if the central substituent is a 4-chlorophenyl group, photoinduced chloride elimination occurs.

During the course of our work in the photochemistry of resonance-stabilized carbanions,[1] we have been seeking a model that adequately accounts for the diversity of reactions which occur from the excited-state manifold. One such model which seems readily to describe the reaction pathways observed in such systems is contained in the notion of "charge redistribution", or, less precisely, "intramolecular charge transfer". If, for instance, we consider a prototypical odd-alternant hydrocarbon anion such as the allyl anion, we note that in the Hückel molecular orbital description the negative charge is localized at the terminal carbons, corresponding to the qualitative valence bond model and reflecting population of the antisymmetric nonbonding molecular orbital (NBMO). In the one-electron approximation, formation of the first excited state corresponds to removal of an electron from the nonbonding antisymmetric MO and population of the symmetric antibonding MO, and thus a "redistribution of charge" results (see Figure 1). More importantly, this change in symmetry of the highest occupied molecular orbital upon photoexcitation is a general property of odd-alternant hydrocarbon anions, and substitution by aryl groups to yield more reasonably accessible carbanions does not change this essential feature.

The chemical consequences of charge redistribution in photoexcited carbanions are manifold. We have already observed that 2-chloro-1,3-diphenylindenyl anion, formally an allyl anion with a 1,3-benzo bridge, undergoes facile chloride expulsion in the excited state,[1,2] reflecting the increased charge density at C-2. Similarly, 1,3-diphenylpropenyl anion undergoes facile photochemical *E,Z* isomerization,[3] a result which may reflect the decreased bond order in the excited state associated with population of the symmetric antibonding orbital. In order to more carefully define the effect of such charge redistribution on anion photoreactivity, we elected to design an allyl system in which ground-state effects would be minimal and excited-state effects would dominate. Our chosen substrates were 2-aryl-1,3-diphenylpropenyl anions in which the 2-aryl substituent was phenyl, *p*-biphenylyl, 2-naphthyl, and *p*-chlorophenyl, i.e., 1,2,3-triphenylpropenyl anion (TPP), 1,3-diphenyl-2-(*p*-biphenylyl)propenyl anion (DBP), 1,3-diphenyl-2-(2-naphthyl)propenyl anion (DNP), and 1,3-diphenyl-2-(4-chlorophenyl)propenyl anion (Cl-TPP).

The way in which ground-state effects are minimized and excited-state effects maximized can best be understood by an appeal to the Hückel molecular orbitals and the use

Table I. Bond Orders and Charge Densities for Photoexcited Allyl Anions[a]

| property | anion | | |
	TPP	DBP	DNP
1,2 bond order	0.52 (0.61)	0.54 (0.61)	0.57 (0.61)
C-1,3 charge density	−0.63 (−1.0)	−0.40 (−1.0)	−0.29 (−1.0)
C-2 charge density[b]	−0.37 (0.0)	−0.60 (0.0)	−0.71 (0.0)
E (LUMO), β	0.64	0.56	0.54
$E_{1/2}$ (substituent)[c]	−3.3	−2.70	−2.50
$E_{1/2}$ (*)[c,d]	−2.43	−2.25	−2.21

[a] Figures in parentheses represent ground state values. [b] Includes charge on central substituent. [c] In V vs. SCE. [d] Calculated from Hückel coefficients using method.

of a perturbation treatment. Considering 1,3-diphenylpropenyl anion, we note that the charge distribution in the ground state is determined by the coefficients of the NBMO, which have nonzero values at C-1, C-3, and the ortho, para positions of the phenyl groups. Since the NBMO is antisymmetric and has a node at C-2, introduction of substituent at C-2 does not change that charge distribution; the perturbation will be zero. Provided that steric effects are comparable, we would expect the ground-state properties of the anions which depend on the distribution of charge to be indistinguishable. The substituents were chosen so as to have similar steric environments.

In the excited state, the symmetry of the allyl π_s* orbital allows mixing with the π* orbital of the substituent. The resultant singly occupied molecular orbital has an energy which depends upon the energy of the π_s* orbital in the substituent (see Figure 2 and Table I). This result is confirmed by Hückel calculation. Thus lowering the reduction potential (π* energy) of the 2-substituent of a 2-aryl-1,3-diphenylpropenyl anion should have the following effects on its photochemistry: (1) an "intramolecular electron transfer" into the central aryl ring, (2) a decreased intermolecular electron-transfer efficiency, and (3) an increased *E,Z* isomerization efficiency. We now report that these predictions coincide in every way with experiment.

Results

Synthesis of Reactants and Potential Photoproducts. The requisite 2-aryl-1,3-diphenylpropenes were

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(1) For leading references, see: Tolbert, L. M.; Siddiqui, S. *J. Am. Chem. Soc.* **1984**, *106*, 5538.
(2) Tolbert, L. M.; Siddiqui, S. *J. Am. Chem. Soc.* **1982**, *104*, 4223.
(3) (a) Parkes, H. M.; Young, R. N. *J. Chem. Soc., Perkin Trans. 2* **1978**, 249. (b) Bushby, R. J. *Ibid.* **1980**, 1419.
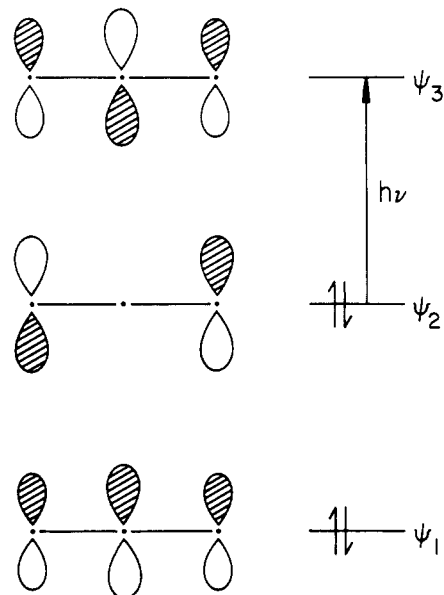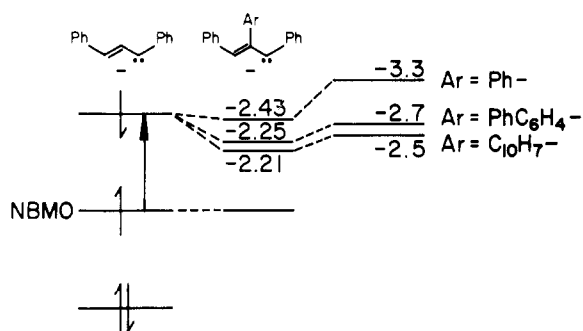
Figure 1. Allyl anion MO's.

Figure 2. Perturbation by central substituent. Numbers in V vs. SCE were obtained by using the method of Streitwieser: Streitwieser, A., Jr., "Molecular Orbital Theory for Organic Chemists"; Wiley: New York, 1961. The value used for benzene is the extrapolation by Gerson: Gerson, F.; Ohya-Nishiguchi, H.; Wylder, C. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 552.
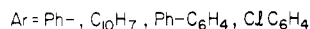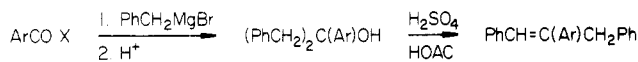

Figure 3. Synthesis of propenes.

synthesized by treatment of the required methyl arenecarboxylate or arenecarbonyl chloride with 2 equiv of benzylmagnesium bromide in tetrahydrofuran, followed by dehydration of the resulting carbinol with 20% sulfuric acid in acetic acid (see Figure 3). All compounds were crystalline solids, gave satisfactory elemental analyses, and were configurationally pure *E* isomers (see Experimental Section).

From our previous studies on carbanion photochemistry, we anticipated two types of photoproducts from irradiation of the allyl anions. One type involves a photooxidation (electron ejection) followed by radical dimerization, the other a photomethylation when Me_2SO is the solvent. Synthesis of both types of potential photoproducts was readily achieved. The former was accomplished by oxidation by nitrobenzene of the anion formed by deprotonation of the appropriate hydrocarbon in tetrahydrofuran using lithium diisopropylamide base. The other was accomplished by methylation of the appropriate anion in Me_2SO with methyl iodide. In the latter case, subsequent
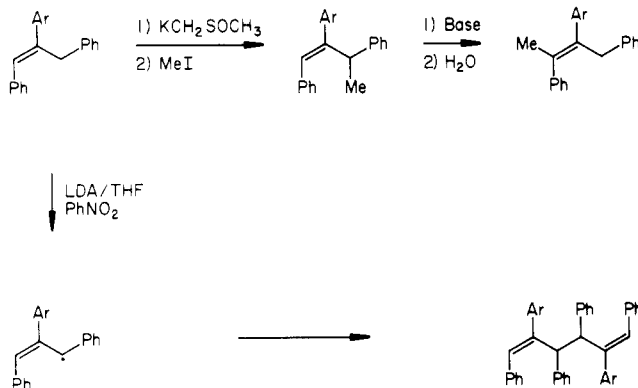

Figure 4. Synthesis of photomethylated products and oxidative dimers.

Table II. Absorption Spectra (nm) of the Allyl Anions

compd	solvent	cation	max	max
TPP	Me_2SO	K^+	548	2.8×10^4
	THF	Li^+(LDA)	548	
	THF	Li^+(n-BuLi)	548	
	hexane	Li^+(n-BuLi, TMEDA)	485	
DNP	Me_2SO	K^+	528	3.1×10^4
	THF	Li^+(LDA)	528	
	hexane	Li^+(n-BuLi, TMEDA)	522, 455	
BDP	Me_2SO	K^+	578	1.4×10^4
	THF	Li^+(LDA)	578	
	hexane	Li^+(n-BuLi, TMEDA)	472	

treatment of the initially formed product with additional base isomerized the product to the more stable tautomer (see Figure 4). For each of the three anions, yields of both methylated products and oxidative dimers were nearly quantitative, although invariably a mixture of geometric isomers was obtained (see Experimental Section).

Preparation and Characterization of Anion Solutions. Solutions of the anions TPP, DNP, and DBP were prepared in Me_2SO, tetrahydrofuran, hexane, and liquid ammonia by treatment of the conjugate acid with base. C1-TPP was prepared in Me_2SO only. In each case the identity of the counterion was controlled by convenience of generation or utilization of the requisite base. In Me_2SO, where counterion effects can be assumed to be negligible,[4b] the base employed was potassium (methylsulfinyl)methide ("dimsyl"). In tetrahydrofuran, lithium diisopropylamide (LDA) or n-BuLi was used, which resulted in the solvent actually being a tetrahydrofuran–hexane mixture. In hexane, butyllithium–tetramethylethylenediamine (TMEDA) was employed, and in liquid ammonia, sodium amide generated in situ. In each case, addition of base produced an immediate deep coloration of the solution from brown-red to purple as a function of solvent system and, presumably, degree of ion pairing. The spectral properties of the solutions so prepared are shown in Table II.

Irradiations were carried out at 10^{-2} M to 10^{-4} M anion concentration. Solutions for NMR analyses were prepared similarly, but with deuterated solvents and at much higher concentrations (0.1–1.0 M).

NMR Studies. In order to determine the validity of the Hückel model for the nodal properties of the odd-alternant hydrocarbon anions, the NMR spectra of anions TPP, DBP, and DNP were obtained. Treatment of Me_2SO solutions of the hydrocarbons with potassium (methylsulfinyl)methide ("dimsyl") produced immediate formation

(4) (a) Tolbert, L. M.; Ali, M. Z. *J. Org. Chem.* **1982**, *47*, 4793. (b) Matthews, W. S.; Bares, J. E.; Bartness, J. E.; Bordwell, F. G.; Cornforth, F. J.; Drucker, G. E.; Margolin, Z.; McCallum, R. J.; McCollum, G. J.; Vanier, N. R. *J. Am. Chem. Soc.* **1975**, *97*, 7006.

Table III. ^{1}H and ^{13}C NMR and Data[a] for the pK_a Allyl Anions

	TPP	DBP	DNP
pK_a	28.8 ± 0.3[b]	28.9 ± 0.3[b]	29.2 ± 0.3
[1]H (ppm) (1,3)	4.58 (br) allylic	4.70 (br) allylic	4.68 (br)
	5.75–5.98, allylic	5.83–6.07, para	5.85–6.08, para
	6.01–6.25, ortho	6.10–6.37, ortho	6.11–6.35, ortho
	6.32–6.65, meta	6.40–6.70, meta	6.45–6.72, meta
	6.88–7.25, neutral	7.10–7.73, neutral	7.18–7.32, neutral
[13]C (ppm) (1,3)	93.0,[c] vinyl	93.0, vinyl	vinyl[d]
	111.96, para	112.17, para	112.06, para
	122.48, 124.98, 127.75, 128.21, 128.87, 143.94, 144.81	122.48, 124.34, 125.95, 126.88, 127.08, 127.52, 127.87, 129.34, 131.73, 133.29, 144.07, 148.03	122.64, 125.32, 125.46, 125.92, 126.20, 126.36, 126.51, 126.78, 127.03, 127.32, 127.60, 127.99, 128.26, 128.35, 128.43, 128.79, 128.99, 129.22, 129.47, 136.69, 138.89, 139.44, 140.50

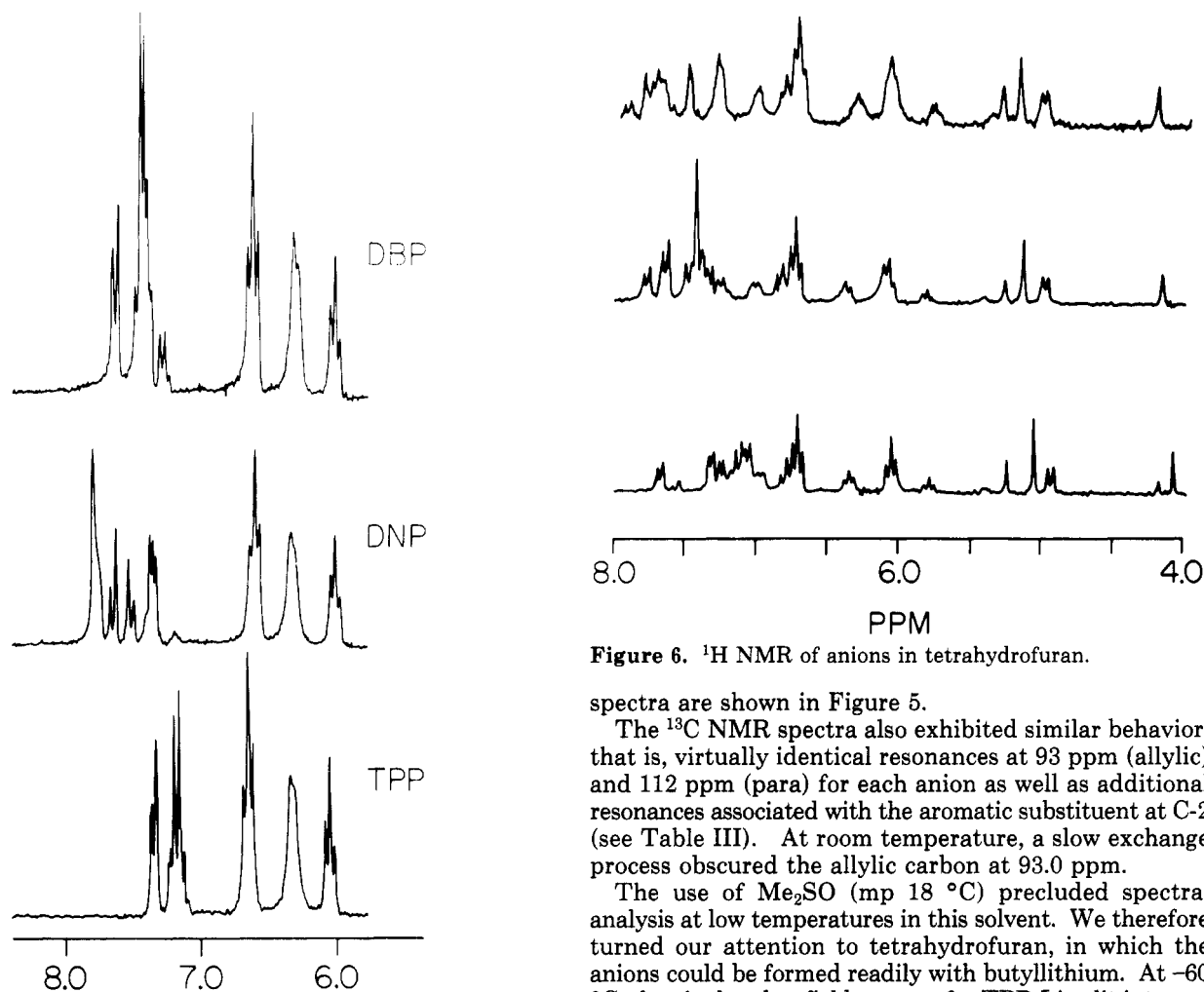[a] Ambient temperature.　[b] Average of five runs.　[c] The number reported previously[4a] was in error.　[d] Unobserved.

Figure 5. ^{1}H NMR of anions in Me_2SO.

Figure 6. ^{1}H NMR of anions in tetrahydrofuran.

of a deep red to violet color. The ^{1}H NMR spectra of these solutions exhibited considerable broadening at room temperature, consistent with the intervention of slow exchange phenomena. At elevated temperature (70 °C), the signals sharpened considerably and allowed a straightforward analysis of the spectra. Each spectrum consisted of two sets of resonances. One set contained the resonances associated with the anionic 1,3-diphenylpropenyl framework, i.e., the typical triplet–doublet–triplet pattern of a phenyl carbanion at δ 6.0–6.7 as well as the allyl vinyl peak at δ 4.6–4.7. This pattern was identical in coupling constants and chemical shift for all three anions. The second set consisted of an aromatic multiplet at δ 6.9–7.7 with a pattern characteristic of the individual aromatic. The

spectra are shown in Figure 5.

The ^{13}C NMR spectra also exhibited similar behavior, that is, virtually identical resonances at 93 ppm (allylic) and 112 ppm (para) for each anion as well as additional resonances associated with the aromatic substituent at C-2 (see Table III). At room temperature, a slow exchange process obscured the allylic carbon at 93.0 ppm.

The use of Me_2SO (mp 18 °C) precluded spectral analysis at low temperatures in this solvent. We therefore turned our attention to tetrahydrofuran, in which the anions could be formed readily with butyllithium. At –60 °C, the vinyl and upfield protons for TPP-Li split into two distinct sets as reported by Boche,[5] corresponding to the freezing out of exchange between the *E,E* and *E,Z* conformations. Curiously, the ortho protons of the phenyl groups for the *E,E* conformer were observed as two doublets, one at δ 4.9 and one at δ 7.7–7.8, corresponding to endo protons in the shielding region and exo protons in the deshielding region of the opposite aromatic ring in this sterically congested conformation (see Figure 6). With slight differences in ratio of the two conformers, this pattern persisted for naphthyl- and biphenylyl-substituted species DNP-Li and DBP-Li, with, again, additional resonances associated with the substituent (see Figure 6).

(5) Boche, G.; Buckl, K.; Martens, D.; Schneider, D. R. *Liebigs Ann. Chem.* 1980, 1135.

pK_a Studies. The equilibrium pK_a's of the three hydrocarbons TPP-H, DBP-H, and DNP-H were determined using a modification[4a] of Bordwell's method.[4b] Specifically, Beer's law plots in the visible absorption region of each anion were carried out in 1-nm increments over the entire spectrum. A least-squares analysis at each wavelength allowed determination of the molar absorptivity spectrum. Me$_2$SO solutions of mixtures of the unknown hydrocarbon and an indicator standard (biphenylyldiphenylmethane) were treated with 0.5 equiv of dimsylpotassium. The resulting absorption spectrum was subjected to a spectral decomposition using the digitized absorption spectra of the pure anions and the concentration of each anion determined by least-squares analysis. From the known concentration of each species and the reported pK_a of biphenylyldiphenylmethane,[4] the pK_a of each hydrocarbon was calculated and reported in Table I. Also reported in Table II are the absorption maxima of the three anions.

Preparative Irradiations. Solutions of each anion were prepared in Me$_2$SO by using potassium dimsyl and Schlenk techniques in an argon atmosphere. Irradiations were carried out externally by using a Hanovia 450-W medium-pressure mercury arc lamp and a solution filter consisting of either 0.1 M K$_2$CrO$_4$ solution adjusted to pH 10 with NH$_4$OH (filter A), or 10^{-3} M BiCl$_3$ in 1 M HCl (filter B). Filter A effectively excluded all wavelengths below 450 nm, and filter B excluded all light below 350 nm. Irradiations times ranged from 20 min to 24 h. The major products from 1-h irradiation of chlorophenyl anion 4 were its reduction product TPP-H in 30% yield and the radical dimer of TPP, 1,2,3,4,5,6-hexaphenyl-1,5-hexadiene [(TPP)$_2$], in 60% yield. In contrast, short-term irradiation of hydrocarbon anions TPP, DBP, and DNP produced a mixture of *E,Z* isomers whose composition varied with irradiation time and identity of the anion (see below). If an irradiated solution was allowed to stand for 2–4 h after the irradiation and then quenched, the *Z/E* ratio returned to the unirradiated value. Long-term irradiations (24 h) followed by quenching produced a 5% yield of the starting hydrocarbon mixture as well as the products of photomethylation in 50–60% yield and the oxidative dimers in 1–7% yield.

Irradiations were also carried out in tetrahydrofuran. Solutions of the anions TPP-Li, DBP-Li, and DNP-Li (10^{-3} M) were prepared in tetrahydrofuran with *n*-butyllithium and irradiated with the identical light source and filter solution as above. Even after prolonged irradiation at room temperature, no change was noted in the observed *E,Z* ratio of 0.20–0.40. Irradiations were also carried out at low temperature on TPP and DBP. Again, no significant change in *E,Z* ratio was observed.

Solutions of TPP-Li, DBP-Li, and DNP-Li in hexane were irradiated from 8–10 h at 0 °C, quenched with MeOH at 0 °C, and analyzed by gas chromatography. Starting materials were recovered nearly quantitatively, and the *E/Z* ratio was the same before and after irradiation (see Table IV).

The photochemistry of DBP-Na and DNP-Na in liquid ammonia was complicated by ground-state chemistry. Thus a freshly prepared solution of DBP-Na in liquid ammonia was allowed to stand for 30 min before quenching. Evaporation of the solvent and isolation of the products by thin layer chromatography yielded starting hydrocarbon (3%), oxidative dimer (DBP)$_2$ (38%), 2-(4-biphenylyl)styrene (20%), and unidentified polar compounds (32%). Similarly, DNP-Na in liquid ammonia produced unreacted DNP-H (3%), dimer (DNP)$_2$ (32%), 2-(2-naphthyl)styrene (24%), and unidentified polar com-

Table IV. Photochemical Properties of 1,3-Diphenyl-2-arylallyl Anions

property	solvent	anion		
		TPP	DBP	DNP
Z/E (after quenching				
before irrad	Me$_2$SO	0.37	0.30	0.86
4-h irrad	Me$_2$SO	0.38	0.56	0.69
10-h irrad	Me$_2$SO	0.40	0.82	0.36
before irrad	THF	0.20	0.38	0.32
after irrad	THF	0.21	0.40	0.36
before irrad	NH$_3$	0.50		
after irrad	NH$_3$	0.25		
after irrad (C$_{10}$H$_8$)	NH$_3$	0.05		
before irrad	C$_6$H$_{14}$	0.42	0.41	0.54
after irrad	C$_6$H$_{14}$	0.40	0.42	0.54
% *E* (added stilbene)	THF	0.86	0.08	0.11
photomethylation QY,[a] 24-h irrad	Me$_2$SO	1.3×10^{-3}	1.4×10^{-3}	1.5×10^{-3}

[a] QY, quantum yield.

pounds (26%). In each case, the identity of the known products was established by comparison with independently prepared materials. Also, the polar fraction did *not* contain benzylamine.

Only triphenylpropenyl anion TPP-Na was stable in liquid ammonia. Irradiation of TPP-Na in liquid ammonia at reflux for 45 min produced a 90% yield of TPP-H after quenching with a *Z/E* ratio of 0.25, as well as ca. 3% of dimer TPP$_2$. A control maintained under the same conditions without irradiation returned a quantitative yield of TPP-H with a *Z/E* ratio of 0.49. An identical solution irradiated with naphthalene present at 1.6×10^{-4} M produced a *Z/E* ratio of TPP-H of 0.05, as well as ca. 20% of dimer (TPP)$_2$.

Merry-go-round Irradiations. In cases where permanent photochemistry was in evidence, relative quantum yields were determined by using a merry-go-round apparatus and the identical-irradiation train. Under these conditions the only wavelengths captured by the samples were the 546- and 578-nm mercury lines. Additionally, the relative rate of electron-transfer-sensitized isomerization of *cis*-stilbene was determined.

Equimolar 25-mL solutions of anions TPP, DBP, and DNP–Me$_2$SO were prepared as above and then irradiated for 10 h, with aliquots removed and analyzed at 0, 4, and 10 h. The *Z/E* ratios of propenes are reported in Table IV. Similar solutions irradiated for 24 h at higher lamp intensity exhibited extensive methylation and dimerization, with yields of those products reported in Table IV.

Equimolar (5×10^{-2}) 10-mL solutions of anions TPP-Li, DBP-Li, and DNP-Li in tetrahydrofuran were prepared as above, but in addition were treated with 0.50 mmol of *cis*-stilbene. The solutions were irradiated (filter B) for 30 min, quenched, and analyzed by gas chromatography. The yield of *trans*-stilbene in each case is reported in Table IV. A control experiment involving irradiation of *cis*-stilbene without anion present produced no detectible yield of *trans*-stilbene.

Discussion

Ground-State Properties. The chemical and NMR properties of the three hydrocarbon anions are in remarkable accord with the qualitative Hückel molecular orbital description. Thus the proton chemical shifts of anions can be grouped into two sets. One set includes the 1,3-diphenylpropenyl anion moiety and exhibits downfield shifts for protons on the "starred" carbon atoms for these odd-alternant hydrocarbon anions. The other set includes the protons on the C-2 substituent and exhibits little downfield shift in comparison with the parent hydro-
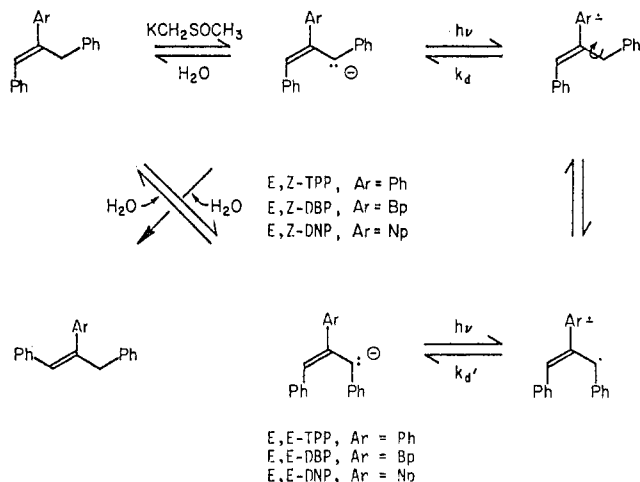
Figure 7. Excited-State *E,Z* isomerization of anions.

Figure 8. Electron-transfer-induced isomerization of *cis*-stilbene.

carbon. Since carbon chemical shifts are reliable guides for charge density for sp^2 hybridized carbanions, the fact that both proton and carbon chemical shifts for the carbanionic carbons are identical while the C-2 substituent protons and carbons exhibit little downfield shift is in accord with our expectations based on the nodal properties of the allyl anion MO's. Moreover, the pK_a's of the hydrocarbons are the same within experimental error, further substantiating the lack of a ground-state effect of the C-2 substituent on the anionic properties.

One reason for choosing the particular substituents of this study was to minimize differences in steric effects. The fact that the ratio of *E,E* to *E,Z* conformers is relatively constant for the three anions substantiates this choice. Remarkably, the more bulky 2-naphthyl group actually *increases* the proportion of *E,Z* isomer. In this case, secondary orbital interactions, e.g., charge transfer, may stabilize a cis disposition of the naphthyl and one phenyl group.

Although the ^{1}H NMR line broadening at room temperature in Me$_2$SO precludes the determination of conformer distributions and their role in the hydrocarbon isomers formed upon protonation in that solvent, the analysis of the conformer distributions in tetrahydrofuran at low temperature provides a reliable guide to the protonation behavior. Thus the proportion of *E,Z* conformer ranged from 50% to 60%. Since protonation of the *E,E* conformer leads only to (*E*)-propene, while protonation of the *E,Z* conformer leads to (*E*)- or (*Z*)-propene depending upon protonation site, the yield of (*Z*)-propene produced upon protonation provides an estimate of the proportion of *E,Z* conformer present in solution. Thus if protonation at all sites is statistical, a 50:50 ratio of conformers will lead to 25:75 ratio of propene isomers, i.e., $Z/E = 0.33$. This is very close to the ratio observed for protonation of unirradiated samples in all solvents used.

Excited-State Properties. The formation of propenes from quenching of irradiated solutions of anions TPP, DBP, and DNP which differ in Z/E ratio before and after irradiation reflects a change in the conformer ratio of the anions upon irradiation (see Figure 7). Thus an increased (or decreased) proportion of *E,Z* anion conformer in solution upon irradiation results in an increased (or decreased) Z/E ratio of propenes upon quenching. The curious fact that DNP exhibits opposite isomerization behavior may again reflect the intervention of secondary orbital interactions. Irradiation of TPP also produced similar isomerization behavior in liquid ammonia, whereas irradiation of all three anions in tetrahydrofuran produced
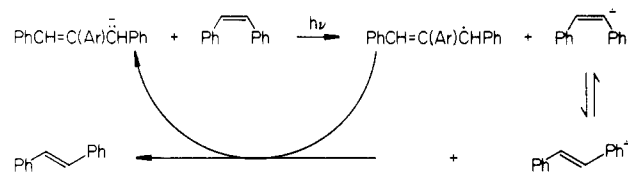
no permanent photochemistry. This is analogous to the behavior of 1,3-diphenylpropenyl anion (DPP) reported by Young and Bushby.[3] That is, ground-state isomerization of DPP is too fast in tetrahydrofuran to allow competitive photochemical isomerization, presumably because of the intervention of ion pairs in tetrahydrofuran.

The photomethylation of TPP, DBP, and DNP in Me$_2$SO is apparently a further example of electron-transfer-induced formation of methyl radicals which undergo alkylation of ground-state anions. This mechanism has been subjected to extensive scrutiny by us previously.[6]

The cis–trans isomerization of *cis*-stilbene when the olefin is added to a solution of anion prior to irradiation is most readily accounted for by an electron-transfer mechanism. Thus electron transfer to olefin from photoexcited anion produced *cis*-stilbene radical anion, which undergoes the known isomerization to *trans*-stilbene radical anion (see Figure 8). Other less appealing mechanisms can be postulated. One pathway, which would involve proton transfer from stilbene to form a configurationally unstable vinyl anion, is untenable under these reaction conditions. The strongest base present in solution is the hydrocarbon anion, yet control experiments indicated no isomerization of stilbene even with the stronger base potassium dimsyl. Moreover, similar experiments by Fox using the more basic cyclooctatetraene dianion indicated no isomerization by this mechanism.[7] Other mechanistic possibilities involving formation of stilbene excited states either by direct absorption or sensitization are excluded either by control irradiation without anion or by the low energies of the anionic states involved. Finally, hydrocarbons of similar reduction potential have been shown to quench the electron-transfer photochemistry of another anion, triphenylmethyl anion.[6a] Thus the electron-transfer route is the only plausible mechanism.

The photoreduction of C2-TPP is consistent with an intramolecular electron-transfer mechanism to form an excited state which is like a radical anion with respect to the chlorophenyl ring. Chloride expulsion leads to formation of an aryl radical which can undergo further hydrogen atom abstraction or reduction under these reducing conditions. In fact, C2-TPP undergoes a rich and varied chemistry in the presence of a variety of nucleophiles, which is the subject of a separate article.[8]

The photochemical isomerization behavior of all four anions substantiates the qualitative HMO picture discussed above in which charge density migrates from the C-1 and C-3 benzyl moieties to the C-2 benzyl moiety. The fact that TPP isomerizes *least* efficiently despite a modestly larger excited-state C-1,2 bond order (Table I) suggests that excited-state stabilization plays the dominant role. An alternative explanation involves the phenomenon of "optical pumping". That is, if the conformers of the individual anions have different absorption properties, they may absorb light unequally, thus leading to different

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populations of isomers and an apparent difference in reactivity. This would require an accidental equality of photoreactivity of the two conformers of TPP, since little change in the isomer distribution is produced upon irradiation. However, in a study of the structurally related 1,3-diphenylpropenyl anions, Bushby synthesized derivatives which were fixed in *E,E*, *E,Z*, and *Z,Z* conformations.[9] Remarkably, little difference in the absorption characteristics of these conformationally fixed anions was observed. Moreover, if optical pumping were involved, the direction of the electron-transfer reactivity should be the same as the isomerization behavior. In fact, the opposite order is observed. The same effect which decreases the excited-state oxidation potential makes the excited state of the species a less powerful reducing agent. Consequently, their ability to form stilbene radical anions is decreased. It is instructive to compare the reduction potentials calculated from the Hückel π^* coefficients of the anions (Table I) with the measured reduction potential of stilbene (−2.2 V vs. SCE). In the case of DNP and DBP, the electron transfer is predicted to be isoergic, whereas the electron transfer from TPP is significantly exoergic.

In contrast to the isomerization behavior, the photomethylation behavior is, within experimental error, independent of anion structure. This result is most readily understood on the basis of an electron photodetachment. That is, rather than forming of an anionic excited state, some of the incident photons eject electrons and produce $Me_2SO^-\cdot$, which undergoes bond homolysis to produce methyl radical in accord with our published mechanism[6] and with the behavior of Me_2SO upon electron capture following γ-radiolysis.[10] We have found that the quantum yield of photomethylation of triphenylmethyl anion exhibits an increased quantum yield at shorter wavelengths, in accord with a photodetachment.[11] Thus the quantum yield of photomethylation of these structurally similar anions is independent of the anionic excited state, which is not formally involved. A related phenomenon is the increased isomerization of TPP upon irradiation with naphthalene in liquid ammonia. Presumably, the naphthalene provides an electron sink for photoexcited electrons, and the isomerization mechanism under these conditions involves bond rotation in the 1,2,3-triphenylpropenyl radical. Coincidentally, the product of radical dimerization [(TPP)$_2$] is significantly increased under these conditions.

Conclusions

The photochemistry of 1,3-diphenyl-2-arylallyl anions is remarkably in accord with the Hückel molecular orbital model. Moreover, the relative efficiencies of *E,Z* isomerization indicate that the excited state, once formed, is bound with respect to electron detachment. This further verifies the use of resonance delocalization to stabilize anionic excited states and allows the use of charge redistribution as an effective model for rationalizing and predicting anionic photoreactivity.

Experimental Section

Materials. All solvents were ACS reagent grade. Organic reagents unless otherwise noted, were obtained from Aldrich Chemical Co., Milwaukee, WI, and were used as received. Dimethyl sulfoxide was purified by following the procedure of

Bordwell[4] and stored over molecular sieves (Linde 4A) under argon. Tetrahydrofuran was dried by distillation from a solution of sodium benzophenone ketyl and collected under argon. Hexane was first purified by treatment with concentrated sulfuric acid and then distilled over calcium hydride. Diisopropylamine (Aldrich) was dried by reflux over calcium hydride and collected just prior to use. *n*-BuLi (1.6 M in hexane) was used without further purification. Lithium diisopropylamide (LDA) was made following the procedure of Newcomb and Ford.[12] Potassium dimsyl was prepared as previously described.

Analyses. Unless otherwise stated, all ^{1}H NMR spectra were recorded on a Varian XL-200 or EM-390 spectrometer and are reported in ppm downfield from internal tetramethylsilane (δ). UV spectra were recorded on a Beckman Model 26 spectrometer. Mass spectra were obtained from a Hitachi Perkin-Elmer RMU-7 double-focusing mass spectrometer. Melting points were taken on a hot stage apparatus and are uncorrected. Gas chromatographic analyses were performed on a Varian 3700 gas chromatograph with flame ionization detector using μ Partisorb OV-101 or OV-17 glass columns (2 mm × 6 ft). For quantitative analysis, a weighed amount of a standard was added to the product mixture, and the relative peak areas of the product and standard were measured with a Hewlett-Packard Model 3390A integrator. The relative molar responses of product and standard were determined independently by measuring the peak areas of a mixture of weighed authentic product and weighed standard. Elemental analysis were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Manipulations. Apparatus and nonvolatile materials were degassed repeatedly by evacuating and purging at least three times with argon. Solvents were transferred by reaching through the bore of a 4-mm three-way stopcock with the needle of a degassed syringe while a constant stream of argon was let in through the side opening of the stopcock. Argon was deoxygenated and dried with use of an Ace-Burlitch inert atmosphere system. For photochemical experiments in solvents other than ammonia, the apparatus was detached from the argon line, and a rubber septum was attached to maintain the inert atmosphere.

Irradiations. All irradiations were carried out with a Hanovia 450-W lamp in a pyrex immersion well (Ace glass, Inc.) positioned adjacent to the reaction vessel. Reaction vessels for nonvolatile solvents were cylindrical vessels, 3 × 20 cm in diameter, with outer water jackets and detachable three-way stopcocks. For liquid ammonia reactions, the reaction vessel was a cylindrical tube (2.5 × 25 cm) attached with a three-way stopcock, an outer jacket with a one-way stopcock which could be connected to a vacuum line, and a flask head with two side arms at a 45° angle one of which was attached to a dry-ice condenser and the other closed by a rubber septum. The apparatus was first evacuated repeatedly and purged with argon. The outer jacket was kept at high vacuum to minimize frosting. The apparatus was kept under argon, an oil bubbler was connected, and gaseous ammonia was passed from a lecture bottle and condensed at the dry-ice condenser. When the desired level of ammonia was attained, the reaction vessel was isolated from the lecture bottle and reactants were added.

Light filtration of the Hanovia lamp was provided by a cylindrical condenser surrounding the immersion well and containing either (a) 0.1 M K_2CrO_4 in a pH 10 buffered (NH$_4$Cl, NH$_4$OH) medium to cut off light below 450 nm or (b) 0.01 M $BiCl_3$ in 0.1 M hydrochloric acid which cut off light below 350 nm. The same configuration was used in merry-go-round experiments, except that a rotating turntable surrounding the immersion well was used to hold the samples.

(*E*)-1,2,3-Triphenylpropene (TPP-H). 1,2,3-Triphenylpropene (TPP-H) was prepared by acetic acid/sulfuric acid dehydration of 1,2,3-triphenyl-2-propanol obtained via a Grignard synthesis. Recrystallization from ethanol gave 3.20 g of (*E*)-1,2,3-triphenylpropene (*E*-TPP-H) as a colorless solid, mp 63–64 °C (lit. mp 63–64 °C):[13] NMR (CDCl$_3$) δ 4.01 (s, 2 H), 6.78–7.53 (m, 16 H).

(*E*)-1,3-Diphenyl-2-(2-naphthyl)propene (DNP-H). The synthesis of 1,3-diphenyl-2-(2-naphthyl)propene was achieved by acetic acid/sulfuric acid dehydration of 1,3-diphenyl-2-(2-

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naphthyl)-2-propanol obtained via a Grignard synthesis. Thus, under an argon atmosphere, a stirred solution of 1.10 g (46.0 mmol) of Mg in 50 mL of freshly distilled THF was treated with 5.80 g (46.0 mmol) of benzyl bromide. Methyl 2-naphthoate (3.28 g, 20.0 mmol) in 30 mL of dry THF was added over 45 min at reflux. The reaction mixture was refluxed for 1 h, cooled, and quenched with saturated NH_4Cl at 0 °C. The organic layer was decanted, the salt residue washed with ether, and the combined organic extracts were washed with 5% HCl, 5% $NaHCO_3$, and water. Drying ($MgSO_4$) and solvent removal yielded a pasty solid containing the alcohol (50%), bibenzyl (ca. 40%), and unreacted methyl 2-naphthoate (ca. 10%). Excess bibenzyl and methyl naphthoate were removed by high-vacuum rotary evaporation at 80–90 °C. The residue was treated with 30 mL of 20% sulfuric acid and then heated on a stream bath for 10 min. The hot mixture was poured into water and ether extracted. Chromatography of the extracted residue on a 2.5 × 60 cm column of silica gel (Fisher grade 62) packed in hexane and eluted with hexane (1000 mL) and 1% ether/hexane yielded 2.62 g (35.0%) of (*E*)-1,3-diphenyl-2-(2-naphthyl)propene as a colorless solid, mp 110–115 °C. Recrystallization from ethanol raised the mp to 114–115 °C: NMR ($CDCl_3$) δ 4.15 (s, 2 H), 6.81–7.82 (m, 18 H); MS, *m/z* 320, 229, 165.

Anal. Calcd for $C_{25}H_{20}$: C, 93.75; H, 6.25. Found: C, 93.62; H, 6.28.

1,3-Diphenyl-2-(4-biphenylyl)propene (DBP-H). The synthesis of DBP-H was achieved analogously to DNP-H. Thus, to a solution of benzylmagnesium bromide from 1.21 g (50.0 mmol) of Mg and 8.55 g (50.0 mmol) of benzyl bromide in 50 mL of dry tetrahydrofuran was added 4.76 g (22.0 mmol) of 4-phenylbenzoyl chloride in 30 mL of dry THF. The resulting crude alcohol mixture was dehydrated and chromatographed as before to yield 3.04 g (40.0%) of (*E*)-1,3-diphenyl-2-(4-biphenylyl)propene as a powder, mp 110–115 °C. Further crystallization from ethanol-ether gave needles, mp 118–120 °C: NMR ($CDCl_3$) δ 4.02 (s, 2 H), 6.74–7.61 (m, 22 H); MS 346, 182, 91.

Anal. Calcd for $C_{27}H_{22}$: C, 93.64; H, 6.35. Found: C, 93.57; H, 6.45.

1,2,3-Triphenyl-2-butene (TPP-Me). Under an argon atmosphere, 1,2,3-triphenylpropene (100 mg, 0.37 mmol) dissolved in 4 mL of dry Me_2SO was treated with 1.3 mL of 0.30 M potassium dimsyl (0.39 mmol). After 10 min methyl iodide was added in excess. Potassium dimsyl was again added in excess, the anion allowed to equilibrate for 10 min, and the reaction quenched with water. Extraction with dichloromethane, drying over anhydrous magnesium sulfate, and solvent removal under vacuum yielded a low melting solid. Recrystallization from ethanol afforded 35 mg of 1,2,3-triphenyl-2-butene, mp 45–55 °C, as an *E,Z* mixture: NMR ($CDCl_3$) δ 1.88 (s, 1.5 H, methyl, *E* isomer), 2.20 (s, 1.5 H, methyl, *E* isomer), 3.61 (s, 1 H, allyl, *Z* isomer), 3.90 (s, 1 H, allyl, *E* isomer), 6.79–7.57 (m, 15 H, aromatic); MS, *m/z* 284, 269, 193.

1,3-Diphenyl-2-(4-biphenylyl)-2-butene (DBP-Me). In a similar procedure for the preparation of TPP-Me, 1,3-diphenyl-2-(4-biphenylyl)propene (102 mg, 0.29 mmol) was treated successively with potassium dimsyl, methyl iodide, potassium dimsyl, and water to yield 1,3-diphenyl-2-(4-biphenylyl)-2-butene. Recrystallization from ether yielded 25 mg of 1-methyl-1,3-diphenyl-2-(4-biphenylyl)propene, mp 75–85 °C, as an *E,Z* mixture: NMR ($CDCl_3$) δ 1.90 (s, 1.5 H, methyl, *Z* isomer), 2.16 (s, 1.5 H, methyl, *E* isomer), 3.30 (s, 1 H, allyl, *Z* isomer), 3.90 (s, 1 H, allyl, *E* isomer), 6.71–7.48 (m, 19 H, aromatic); MS, *m/z* 360, 345, 369.

1,3-Diphenyl-2-(2-naphthyl)-2-butene (DNP-Me). In a similar procedure for the synthesis of TPP-Me, 1,3-diphenyl-2-(2-naphthyl)-2-butene was synthesized from 110 mg (0.34 mmol) of 1,3-diphenyl-2-(2-naphthyl)propene. After recrystallization from ethanol the yield was 25.8 mg (22.7%), and the compound melted at 65–75 °C. NMR spectra revealed the presence of both *E,Z* and *E,E* isomers: NMR ($CDCl_3$) δ 2.08 (s, 1.5 H, methyl, *Z* isomer), 2.36 (s, 1.5 H, methyl, *E* isomer), 3.47 (s, 1 H, allyl, *Z* isomer), 3.82 (s, 1 H, allyl, *E* isomer), 6.40–7.67 (m, 17 H, aromatic).

1,2,3-Triphenylpropene Dimer [(TPP)$_2$]. The method of Boche[14] with some modification[15] was used to prepare the radical

dimer of 1,2,3-triphenylpropene. Thus, lithium diisopropylamide (10 mL, 0.10 M) at 0 °C was added to a solution of 1,2,3-triphenylpropene (50 mg) in 10 mL of THF at 0 °C. The anion was allowed to equilibrate at 15 °C for 16 h and then added to a solution of 0.20 mL of nitrobenzene in 100 mL of THF. The purple color disappeared immediately, and the light yellow nitrobenzene solution became light brown. After 2 min, methanol (ca. 3 mL) was added, the brown color disappeared, and the solution became light yellow. The solvent was removed under vacuum, water was added, and the organic layer was extracted with ether. After drying and evaporation, unreacted nitrobenzene was removed at high vacuum (ca. 0.1 torr) to yield a solid residue containing dimer along with <10% starting propene: NMR ($CDCl_3$) δ 4.23 (s, 1 H), 4.35 (s, 1 H), 6.27–7.60 (m, 16 H).

Similarly prepared was 1,3-diphenyl-2-(2-naphthyl)propene dimer [(DNP)$_2$] and 1,3-diphenyl-2-(4-biphenylyl)propene dimer [(DBP)$_2$]. (DNP)$_2$: NMR ($CDCl_3$) δ 4.30 (s, 1 H), 4.36 (s, 1 H), 6.33–8.40 (m, 36 H). (DBP)$_2$: NMR ($CDCl_3$) δ 4.25 (s, 1 H), 4.31 (s, 1 H), 6.70–7.75 (m, 20 H).

Irradiation of 1,3-Diphenyl-2-arylpropenyl Anions in Me_2SO. 1,2,3-Triphenylpropenylpotassium was generated from 150 mg (0.56 mmol) of (*E*)-1,2,3-triphenylpropene in 20 mL of Me_2SO and 5.00 mL of 0.22 M potassium dimsyl. The solution was placed in close proximity to an immersion well containing filter A and then brought to about 95% conversion (ca. 20–24 h). Quenching with water, extraction with ether, drying over anhydrous $MgSO_4$, and concentration in vacuo yielded a low melting solid which was separated by preparative silica gel TLC. This yielded 105 mg (66%) of a mixture of *E* and *Z* 1,2,3-triphenyl-2-butene (TPP-Me) as a low melting solid. The NMR, mass spectrum, and the GC retention time of the compounds were identical with the independently prepared compounds.

A 140-mg (0.44 mmol) portion of (*E*)-1,3-diphenyl-2-(2-naphthyl)propene in 30 mL of Me_2SO was treated with 5.0 mL of 0.28 M dimsylpotassium under argon, and the solution after equilibration for 15 min was irradiated and worked up as above. Preparative silica gel TLC yielded 1,3-diphenyl-2-(2-naphthyl)-2-butene (DNP-Me, 74.1 mg, 50.2%) and 1,3-diphenyl-2-(2-naphthyl)propene dimer [(DNP)$_2$, 8.0 mg, 5.7%].

Following the above procedure, 145 mg (0.42 mmol) of (*E*)-1,3-diphenyl-2-(4-biphenylyl)propene in 30 mL of Me_2SO was treated with 5.0 mL of 0.25 M dimsylpotassium under argon, the solution after equilibration for 15 min was irradiated, and the products were isolated as above. Separation of the extract by preparative TLC yielded 1,3-diphenyl-2-(4-biphenylyl)-2-butene (DBP-Me, 83.6 mg, 53.3%) and the 1,3-diphenyl-2-(4-biphenyl)propene dimer [(DBP)$_2$, 9.0 mg, 6.2%].

Irradiation of 1,3-Diphenylpropenyl Anions in Tetrahydrofuran, Ambient Temperature. Separate solutions of 5.7 × 10^{-3} M TPP, DBP, and DNP each generated from 0.14 mmol of hydrocarbon in 20 mL of THF and 1 mL of 1.6 N *n*-BuLi (in hexane) in four separate 24-mL photolyzing tubes under argon were equilibrated for 3 h. Aliquots were withdrawn before irradiation and after irradiation (0.1 M K_2CrO_4 filter) at 3 h and 24 h and then quenched with 0.2 mL of water and analyzed by gas chromatography. Within experimental error no change in *Z/E* ratio of the hydrocarbons could be detected.

Irradiation of (1,2-Diphenyl-2-arylpropyl)lithium (TPP-Li) in Tetrahydrofuran, Low Temperature. A solution of 30.0 mg (0.1 mmol) of (*E*)-1,2,3-triphenylpropene dissolved in 25 mL of dry THF was cooled to −80 °C by keeping the probe of an immersion cooler (Neslab, CC-100) immersed in methanol inside the cavity of a specially made condenser with ground joint attached to the photolyzing tube. To the solution was added 0.60 mL of TMEDA and, after 10 min, 1.0 mL of *n*-butyllithium. The solution was stirred for 24 h, irradiated for 2 h using filter A, and quenched with 1 mL of precooled methanol (−80 °C). The solution was allowed to warm to room temperature and analyzed by gas chromatography, which indicated a *Z/E* ratio of 0.25 for 1,2,3-triphenylpropene. In a separate control experiment, TPP-Li was generated in the same manner as above and was quenched with precooled methanol after 24 h of equilibration at −80 to −85 °C.

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Gas chromatographic analysis revealed the Z/E ratio of 0.20.

A similarly prepared solution of DBP-Li generated from 23.5 mg (0.07 mmol) of DBP-H, 1 mL of n-BuLi (1.60 mmol), and 0.60 mL (excess) of TMEDA in 30 mL of THF at -80 to -85 °C was irradiated for 7 h with use of filter A. Gas chromatography after quenching at -80 °C (1 mL of methanol) revealed the presence of DBP with an Z/E ratio of 0.20.

A control solution of DBP-Li, allowed to equilibrate for 24 h, quenched with precooled methanol (1 mL, -80 °C), and allowed to warm to ambient temperature revealed an Z/E ratio of 0.23 for DBP.

Irradiation of (1,2,3-Triphenylpropenyl)sodium (TPP-Na) in Liquid Ammonia. The photochemical reaction vessel was charged with 90.0 mg (3.9 mmol) of sodium, 20 mL of liquid ammonia, and a small crystal of ferric nitrate nonahydrate. After the sodium amide formation was complete, 40 mg (0.15 mmol) of 1,2,3-triphenylpropene was added, and the mixture was stirred for 30 min. The solution was then irradiated for 45 min with use of 0.1 M K_2CrO_4 as filter and quenched with excess solid NH_4Cl. The ammonium was allowed to evaporate, and the residue was extracted with 20 mL of ether. Analysis by gas chromatography revealed the presence of starting propene in a Z/E ratio of 0.25. Comparison by TLC also revealed the presence of small amounts of dimer.

A solution identically prepared but with 1.80 mg (0.020 mmol) of naphthalene produced TPP-H with a Z/E ratio of 0.05, along with significantly increased dimer [(TPP)₂] formation. In contrast, an unirradiated solution without naphthalene produced no dimer and TPP-H with a Z/E ratio of 0.49.

(1,3-Diphenyl-2-arylpropenyl)sodium (DNP-Na) in Liquid Ammonia, Dark Reaction. The reaction vessel was charged with 150 mg (6.50 mmol) of sodium, 30 mL of ammonia, and a small crystal of ferric nitrate nonahydrate. After the sodium amide formation was complete, 115 mg (0.36 mmol) of 1,3-diphenyl-2-(2-naphthyl)propene in 10 mL THF was added, and the mixture was stirred for 30 min, keeping the reaction vessel covered with aluminum foil to avoid any light exposure. The color of the solution discharged, and a precipitate formed. The mixture was quenched with excess solid ammonium chloride, the ammonia was allowed to evaporate, and the residue was extracted with 50 mL of ether. Analysis of the volatile extracts by gas chromatography and comparison with authentic material indicated the presence of β-(2-naphthyl)styrene (90%) and starting 1,3-diphenyl-2-(2-naphthyl)propene (10%). However, analysis by TLC also showed the presence of 1,3-diphenyl-2-(2-naphthyl)propene dimer. The compounds were separated by preparative TLC thick layer chromatography to yield 20.0 mg (24%) of β-(2-naphthyl)styrene, mp 140–142 °C (lit.[16] mp 145–146 °C), and 37.0 mg (32%) of (DNP)₂. The products were identified by comparing the NMR, GC retention time, and TLC behavior of the independently synthesized samples. From the preparative TLC 30.2 mg (26%) of polar compounds was also separated, but the compounds were not identified, although comparison with authentic benzylamine indicated its absence.

In a similar procedure DBP-Na yielded 15.0 mg (20.0%) of β-(4-biphenylyl)styrene, mp 218–220 °C (lit.[17] mp 217 °C), 35.0

mg (33.8%) of 1,3-diphenyl-2-(4-biphenyl)propene dimer, and 34.1 mg (32.4%) of unidentified polar compounds.

Relative Quantum Yields. A. Isomerization of 1,3-Diphenylpropenyl Anions in Me₂SO. Separate solutions of 4.80 × 10⁻³ M TPP, DBP, and DNP each generated from 0.21 mmol of hydrocarbon and 1 mL of 0.30 M potassium dimsyl and 24 mL of Me₂SO in three separate 50-mL photolyzing tubes under argon were allowed to equilibrate for 30 min. The solutions were irradiated in the merry-go-round with 0.10 M K_2CrO_4 filter, and aliquots were withdrawn at 0, 4 and 10 h, quenched with 0.3 mL of distilled water, and analyzed by gas chromatography.

B. Photomethylation in Me₂SO. Separate solutions of 5.00 × 10⁻³ M TPP, DBP, DNP, and biphenylyldiphenylmethane generated from 0.15 mmol of hydrocarbon, 3.0 mL of 0.12 M potassium dimsyl and 27.0 mL of Me₂SO in four separate 50-mL photolyzing tubes under argon were allowed to equilibrate for 30 min. The solutions were irradiated in the merry-go-round with filter B and aliquots (2.00 mL) withdrawn at 0, 20, and 40 min, quenched with 0.30 mL of distilled water, and analyzed by gas chromatography. The methylated products were identified by comparing the retention times of authentic samples prepared independently. The GC was calibrated with standard samples. From the independently measured appearance quantum yields of the photomethylation of biphenylyldiphenyl anion (Φ = 0.0065),[11] the quantum yields of methylation of the propenyl anions were calculated.

D. Irradiation of 1,3-Diphenylpropenyl Anions in Hexane. In three separate photolyzing tubes were placed 0.06 mmol of TPP-H, DBP-H, and DNP-H, and the tubes after degassing were purged with argon. To each tube was added 10 mL of dry THF followed by 0.5 mL of TMEDA and 1.0 mL of 1.6 N n-BuLi. The orange red anions were allowed to equilibrate for 6–10 h and irradiated by using 0.1 M K_2CrO_4 filtered light for 8–10 h at room temperature. Each of the reaction mixtures were then quenched with equal amounts of water (1 mL) and analyzed by gas chromatography. The Z/E ratio of the recovered hydrocarbons is shown in Table IV.

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