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REACTIONS FOLLOWING ELECTRON TRANSFER

ORIGINS OF SELECTIVITY IN THE REACTION OF RADICALS WITH CARBANIONS†

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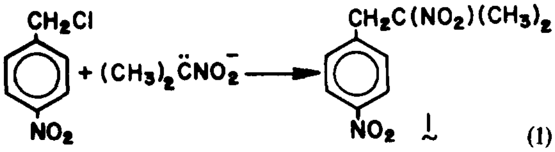
Abstract—The regiochemistry observed upon arylation of ambident carbanions by phenyl radicals can be readily explained by consideration of the site of greatest basicity. Thus 1,3-diphenylindenyl anion is arylated to give predominantly 1,1,3-triphenylindene despite the presumed greater stability of the intermediate leading to 1,2,3-triphenyl indene, that is, the 1,2,3-triphenylisoindene radical anion. This explanation may also account for the preference of C-alkylation rather than O-alklation of nitrocarbanions and for the absence of O-arylation in the $S_{RN}1$ arylation of enolates. The lack of reactivity of other carbanions is rationalized on thermodynamic grounds.

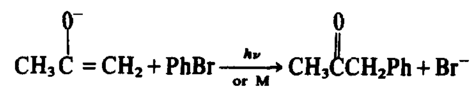
Despite the explosive growth of mechanistic and synthetic organic chemistry over the last three decades, there remain relatively few C–C bond forming reactions in organic chemistry. Our interest in carbanion photochemistry has particularly drawn us to the study of the reaction of radicals with carbanions, not only because such a reaction is an important process following photopromoted electron transfer, but also because the formation of a C–C bond through the reaction of a radical with a carbanion raises the tantalizing possibility of new regio- and chemoselectivities which will expand the array of weapons in the synthetic chemist's arsenal. While a sound mechanistic rationale is available for the reaction of, say, enolates with electrophiles such as alkyl halides, a corresponding rationale for the reaction of carbanions with radicals has not yet been developed except for specialized cases. Our goal in this paper is to present such a rationale.

The reaction of radicals with carbanions to form radical anions was recognized by Russell[1] and Kornblum[2] in 1966 as the key step in the reaction of nitrocarbanions with certain nitroalkyl halides. Thus reaction of 2-nitropropyl anion with *p*-nitrobenzyl chloride proceeds cleanly to give the dinitrobenzylpropane adduct 1 in high yield via addition of the nitrobenzyl radical to the carbanion (eqn 1).



(1)

Subsequently Bunnett recognized this reaction as providing a mechanism for radical mediated nucleophilic aromatic substitution[3] and proposed the name $S_{RN}1$ (eqn 2).

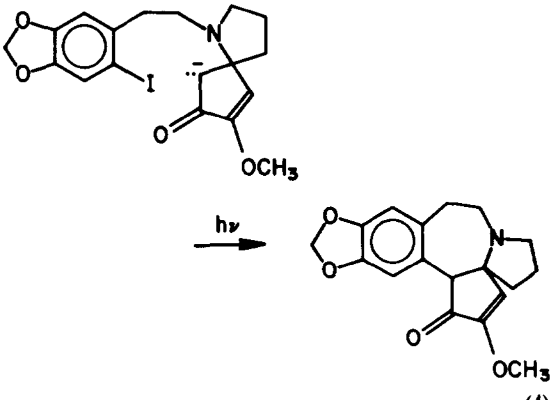


$$CH_3\overset{O^-}{\overset{|}{C}}=CH_2+PhBr\xrightarrow[\text{or M}]{h\nu}CH_3\overset{O}{\overset{\|}{C}}CH_2Ph+Br^- \quad (2)$$

The relevant mechanistic steps are outlined as Scheme 1. From our own work we believe that the first literature example of an $S_{RN}1$ reaction is that of Bergmann,[4] who observed the facile arylation of diphenylmethylsodium with diphenyl sulfoxide but did not recognize the possible free radical mechanism (eqn 3).

$$\underset{\mathbf{2}}{Ph_2CHNa}+Ph_2SO\longrightarrow \underset{\mathbf{3}}{Ph_3CH}+PhSONa \quad (3)$$

Synthetically, this reaction has come to have widespread importance for the α-arylation of enolates and similar nucleophiles,[5] since few convenient alternatives exist. Particularly useful is Semmelhack's application of the intramolecular analogues (eqn 4).[5]



(4)

Two consistent observations about such reactions can be made. First, unlike conventional electrophiles, which commonly produce the results of O-alkylation as a minor if not the major product for ambident carbanions such as enolates, radicals invariably produce the results of C-alkylation. Second, certain carbanions, e.g. dithiane derived carbanions, fail to undergo reaction with radicals at all.[5b] Thus the lack of a clear mechanistic understanding of these observations has hampered further extensions of the $S_{RN}1$ reaction.

An obvious explanation for the reactivity of radicals with ambident nucleophiles is that products are con-

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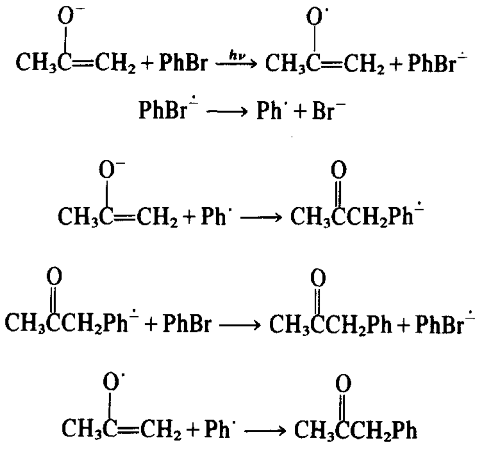
†This is paper No. 4 in our Carbanion photochemistry series. For our previous paper, see L. M. Tolbert, *J. Am. Chem. Soc.* **102**, 6808 (1980).



$$CH_3\overset{O^-}{C}{=}CH_2 + PhBr \xrightarrow{h\nu} CH_3\overset{O^{\cdot}}{C}{=}CH_2 + PhBr^{\dot{-}}$$

$$PhBr^{\dot{-}} \longrightarrow Ph^{\cdot} + Br^-$$

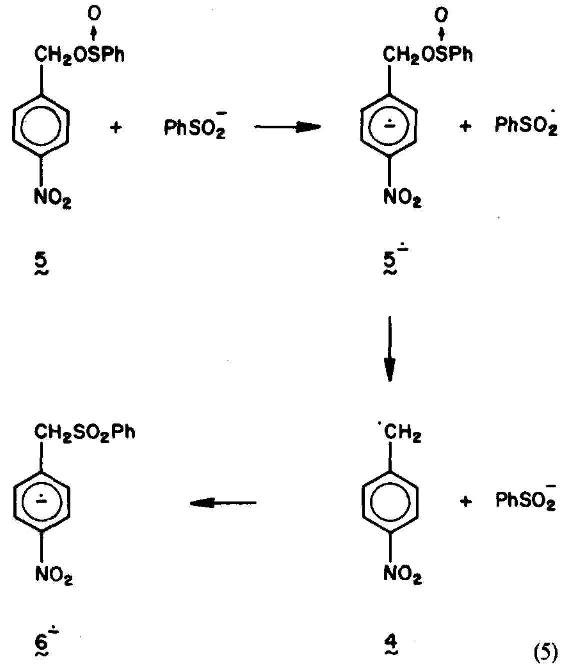
$$CH_3\overset{O^-}{C}{=}CH_2 + Ph^{\cdot} \longrightarrow CH_3\overset{O}{\overset{\|}{C}}CH_2Ph^{\dot{-}}$$

$$CH_3\overset{O}{\overset{\|}{C}}CH_2Ph^{\dot{-}} + PhBr \longrightarrow CH_3\overset{O}{\overset{\|}{C}}CH_2Ph + PhBr^{\dot{-}}$$

$$CH_3\overset{O^{\cdot}}{C}{=}CH_2 + Ph^{\cdot} \longrightarrow CH_3\overset{O}{\overset{\|}{C}}CH_2Ph$$

Scheme 1.

trolled by their stability. That is, C-alkylated carbanions result in radical anions in which the odd electron is localized in a polar C = O or N = O rather than a non-polar C–C or C=N (Fig. 1). An elaboration of this argument is proposed by Kornblum.[6] He views addition of nucleophiles to radicals such as the *p*-nitrotolyl radical **4** as electronically similar to Michael addition (Fig. 2). Thus, although this radical could react with the 2-nitropropyl radical at either oxygen or carbon, reaction at oxygen is reversible and allows equilibration to the thermodynamically more stable C-alkylate. Evidence for this mechanism is offered in the form of sodium benzenesulfinate induced rearrangement of *p*-nitrotolylsulfinate ester **5** to the more stable **6**. Thus, electron transfer from benzenesulfinite produces the radical anion of **5** which undergoes bond homolysis and recombination to give the radical anion of **6** (eqn 5).



(5)

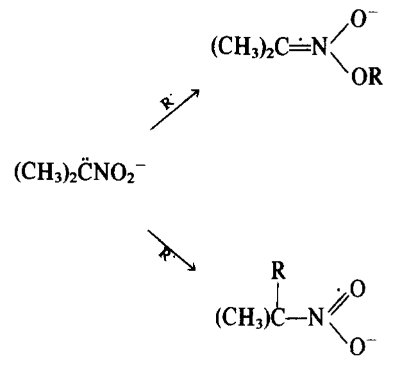


Fig. 1. Cvs O alkylation of ambient carbanions.

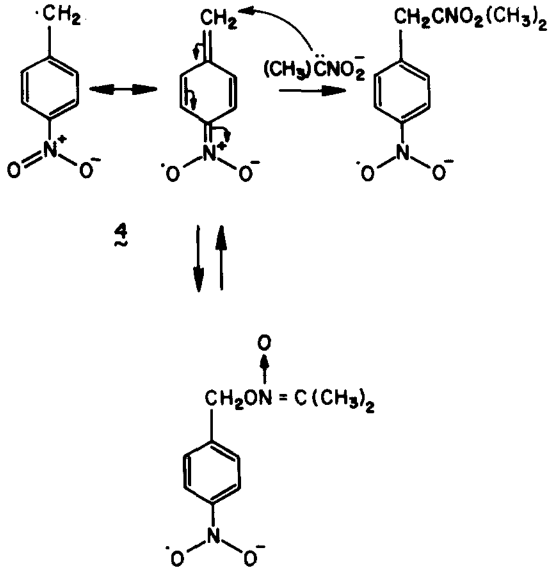


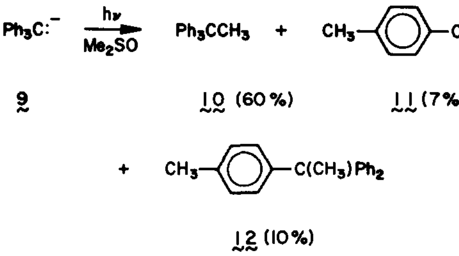
Fig. 2. Free radical addition as Michael reaction.

In any event, this explanation, whether involving direct alkylation at carbon or rearrangement of a preformed intermediate, depends upon the formation of the thermodynamically more stable radical anion. It should be noted that while Kornblum's arguments are persuasive, they are permissive only. That is, while they provide chemical evidence for the feasibility of this pathway and its corresponding mechanistic rationale, the existence of reversibility of itself is not *prima facie* proof for the pathway followed in the actual reaction.

Although $S_{RN}1$ reactions can be initiated either by irradiation, by alkali metal reduction, or by ground state electron transfer, our interest was in the photochemical aspects. In particular, we began studying resonance-stabilized carbanions, since these species would not be subject to complicating electronegativity effects due to heteroatoms and since the results, therefore, should be easier to interpret. We observed the facile photomethylation of 1,1,3,3-tetraphenylpropenyl anion (**7**) in dimethyl sulfoxide (eqn 6)[7].

$$\underset{7}{Ph_2C = CHCPh_2^-} \xrightarrow[Me_2SO]{h\nu} \underset{8(80\%)}{Ph_2C = CHC(CH_3)Ph_2} \qquad (6)$$

Although a mechanism analogous to the $S_{RN}1$ reaction was immediately obvious, we were at first puzzled by what appeared to be the lack of a free radical "fingerprint", i.e. radical-radical recombination products or H atom donor quenching. An early clue that unconventional chemistry was taking place, however, was the discovery that when triphenylmethyl amion was photomethylated, additional products of *para*-methylation were formed (eqn 7).[8]

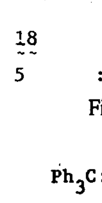


(7)

These products were observed neither from direct alkylation of triphenylmethyl anion with methyl iodide nor from triphenylmethyl phosphite mediated reaction of Me radical with triphenylmethyl Me radical (eqn 8).

$$\underset{13}{\mathrm{Ph_3C^\cdot + CH_3^\cdot}} \longrightarrow \underset{10}{\mathrm{Ph_3CCH_3\,(only)}} \qquad (8)$$

Thus the intervention of the radical anion pathway via the unconventional intermediate **14** was a likelihood. Furthermore, the invariance of *para* to alpha product ratios despite differing anion concentrations indicated that radical anion formation was the dominant feature of the reaction.[8b] When dimethyl sulfoxide was replaced with bromobenzene/THF, the abnormal product **16** became the major one, with the accompanying formation of solvent adduct **17**, clearly establishing the intervention of radicals in that case (eqn 9).[9]



(9)

Thus we were able to propose a mechanism for photoalkylation of resonance-stabilized carbanions which was conceptually similar to the $S_{RN}1$ mechanism but which differed in the absence of chain carrying or radical-radical recombination steps. This mechanism is outlined in Scheme 2.

As part of our mechanistic investigations, we decoupled the photoinitiation step from the free radical alkylation step by carrying out competition studies between triphenylmethyl anion and biphenylyldiphenylmethyl anion. We were surprised to find that triphenylmethyl anion was a better nucleophile than the biphenylyldiphenylmethyl anion toward Me radical, despite the presumed greater stability of the radical anion intermediate derived from the latter. Thus we obtained the first example of selectivity not controlled by the thermodynamics of product stability.[8a] That this result was general was confirmed by similar lack of reactivity on the part of tetraphenylpropenyl anion in competition experiments, and by the apparently greater reactivity of *p*-tolyldiphenylmethyl anion relative to trityl anion (Fig. 3).

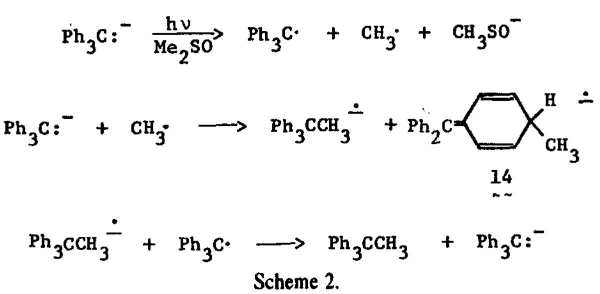
We attributed these results to the preference for alkylation of the more basic carbanion rather than to formation of the more stable radical anion. Our rationale was based upon the fact that the odd electron containing orbital of the radical electrophile becomes the π^* orbital of product. Radical anion stability is a function of the energy of the π^* orbital. However, for exoergonic reactions, this radical anion stability is not perceived until well past the transition state and any stabilizing effects on π^* do not enhance the reaction of the starting materials. In these cases, then, product selectivity is controlled by kinetics which favor alkylation of the more basic, (i.e. nucleophilic) carbanionic center.

If we examine the regiochemistry of typical $S_{RN}1$ reactions in light of these arguments, we see that alkylation or arylation of the more basic site in the ambident nucleophile would also account for the observed results. That is, if we compare the relative stabilities of the conjugate acid of the nucleophile in either the carbon acid or its tautomeric form the greater stability of the carbon acid itself necessitates a greater basicity at carbon, since the derived nucleophile is the same in each case. Enols for instance, are more acidic than corresponding ketones (Fig. 4).

On the basis of this kinetic argument, we would predict C-alkylation rather than O-alkylation by radicals

$$\begin{array}{ccccccc} \mathrm{CH_3C_6H_4\ddot{C}Ph_2^-} & > & \mathrm{Ph_3C:^-} & > & \mathrm{PhC_6H_4\ddot{C}Ph_2^-} & \approx & \mathrm{Ph_2C{=}CH\ddot{C}Ph_2^-} \\ 18 & & 9 & & 19 & & 7 \\ 5 & : & 1 & : & .18 & : & .18 \end{array}$$

Fig. 3. Relative rates of reactivity of carbanions.



Scheme 2.

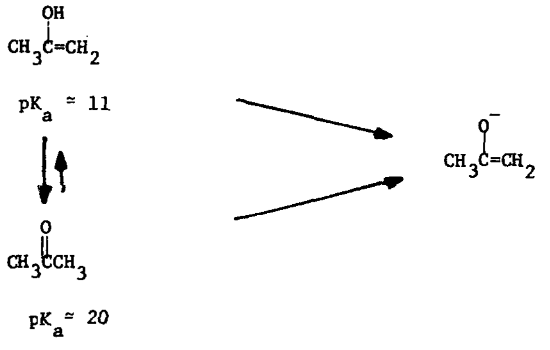
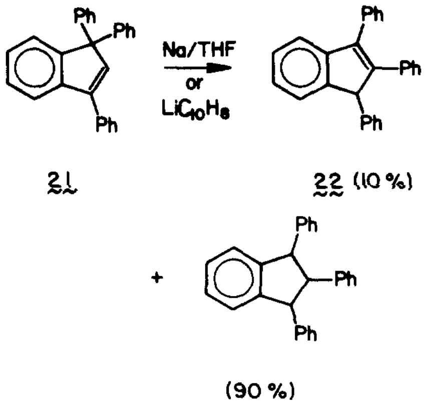


Fig. 4. Comparison of enol and ketone acidities.



21

22 (10 %)

+

(90 %)

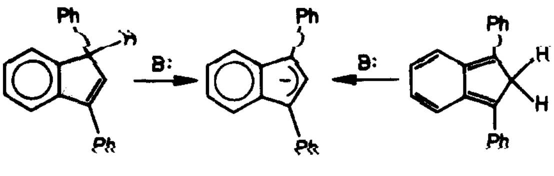
(10)

irrespective of radical anion stability.

In order to determine which of these hypothesis is most predictive, we needed a system in which the two effects gave opposite predictions. That is, control by radical anion stability would lead to one regioisomer and control by site basicity would lead to another isomer. In keeping with our desire to avoid electronegativity effects, we chose a resonance-stabilized carbanion and further required that radical anion stability clearly favor one regioisomer. The 1,3-diphenylindenyl anion (**20**) appeared to be such a carbanion.

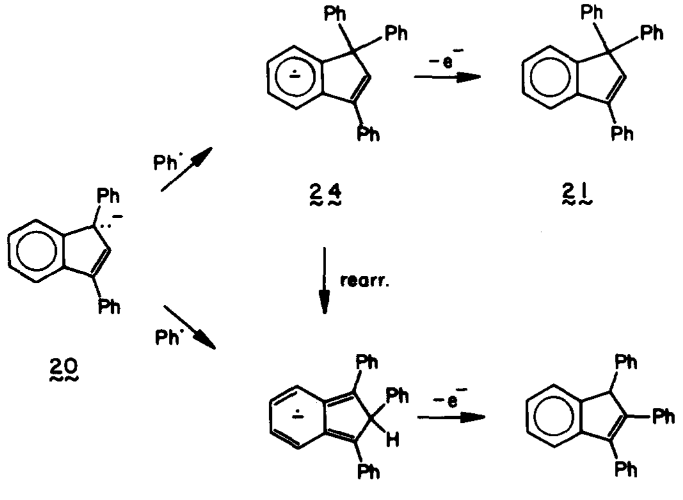
1,2,3-triphenylindene (**22**) (Fig. 5). On the basis of radical anion stability, the 1,2,3-triphenyl isomer should be favored. The presumed intermediate in that reaction is triphenylisoindene radical anion **23**, which is also the rearrangement product from 1,1,3-triphenylindene radical anion **24**. Thus when 1,1,3-triphenylindene is treated with sodium metal in tetrahydrofuran, 1,2,3-triphenylindene is isolated, along with the reduction product 1,2,3-triphenylindane.[10a] We observed a similar reaction when **21** was treated with sodium naphthalenide in THF (eqn 10). If regioselectivity is based upon radical anion stability, then we expect photoarylation of **20** to lead to 1,2,3-triphenylisoindene radical anion followed by electron loss and tautomerization to the neutral **22**.

Arylation at the more basic site of the 1,3-diphenylindenyl anion should lead to the 1,1,3-triphenylindene radical anion. Our rationale is based upon the greater stability of 1,3-diphenylindene compared to 1,3-diphenylisoindene. Although 1,3-diphenylisoindene is unknown, its methylated and phenylated isomers undergo rapid tautomerization even at low temperature to more stable aromatic analogues.[10b] Since the conjugate base of both indene **25** and isoindene **26** are identical, we can conclude that **26** is more acidic than **25** by several pK units (Fig. 6). Thus the 1,3-diphenylindenyl anion provides a clear basis for distinguishing between kinetic and thermodynamic effects in this system.



25 20 26

Fig. 6. Comparison of indene and isoindene acidities.[11]



24 21 20 23 22

Fig. 5. Possible free radical arylation pathways.

RESULTS

The photoarylation of 1,3-*diphenylindenyl anion*

Solutions of 1,3-diphenylindenyl anion were prepared by treating the corresponding conjugate acid **25** with potassium t-butoxide in dimethyl sulfoxide. Irradiation with K_2CrO_4 filtered 450 W Hanovia light (cutoff 450 nm) in the presence of bromobenzene gave moderately rapid consumption of the anion to form both triphenylindenes **21** and **22** in high yield. Alternative procedures using tetrahydrofuran and lithium diisopropylamide gave indenes **21** and **22** along with a solvent adduct **27** and an unknown isomeric hydrocarbon **28** (Fig. 7).

Hydrocarbon **28** disappeared when base concentrations did not exceed indene concentrations and is presumably the benzyne adduct. This adduct retained olefinic and allylic NMR resonances, which implies this product arose from ring arylation. Treatment with di-t-butylnitroxide inhibited formation of indenes **21** and **22**, indicating the free radical pathway was being followed. Significantly, regardless of solvent and conditions, the major product was the kinetic product, 1,1,3-triphenylindene, in a ratio of 5 : 1 over the thermodynamic product, 1,2,3-triphenylindene.

Although we had established the dominant regiochemical pathway, we were still uncertain about the origin of the minor product. 1,2,3-Triphenylindene could have arisen from two alternative pathways. The obvious one is direct attack at C-2 of the 1,3-diphenylindenyl anion. The other pathway involves rearrangement of the direct product of 1-arylation, radical anion **24**, to radical anion **23** via the same pathway followed in dissolving metal induced rearrangement. In order to probe this possibility, we carried out the arylation with bromobenzene-d_5. The direct C-2 arylation would produce the 2-phenyl-d_5 adduct, whereas the ipso arylation rearrangement pathway would produce scrambling of the deuterium label between the C-1 and C-2 phenyl groups (eqn 11).

Isolation of the minor 1,2,3-triphenylindene-d_5 product was carried out as in the undeuterated case. The NMR spectrum showed loss of a peak at 7.05δ, indicating formation of a single deuterated isomer. The mass spectrum, indicated in addition to the parent peaks at at *m/e* 349 peaks at 277 (M-77, 67%) and 267 (M-82, 33%). This compares with percentages of 54% and 61% for the 272 and 267 peaks in scrambled material obtained by photochemical isomerization of 21-d_5. Thus at least a major portion of the 1,2,3-triphenylisomer arises from direct attack at C-2. The presence of the 267 peak (M-82, 33%) is not itself indicative of a minor rearrangement pathway, since 2,3-diphenylindene itself also shows facile loss of phenyl from an unsaturated position.

An alternative method was based upon the fact that rearrangement to radical anion **23** would be first order. Interception of this radical anion by a quencher should reduce the amount of rearrangement product and increase the unrearranged product. Since bromobenzene is the chain carrier for $S_{RN}1$ arylations, we chose it as the electron acceptor as well. Irradiation of 1,3-diphenylindenyl anion in the presence of differing concentrations of bromobenzene gave the product yields and ratios shown in Table 1. Within experimental error the ratios are the same. However, the limiting product yield with increasing bromobenzene concentration indicates that a chain mechanism is not involved, so that the invariance of product ratio with bromobenzene concentration does itself rigorously exclude a rearrangement pathway. Interestingly, the product ratios observed do not conveniently follow Stern–Volmer kinetics, since bromobenzene is consumed in the reaction. We are studying this phenomenon further.

Finally, we note that irradiation of dimethylsulfoxide solutions of 1,3-diphenylindenyl anion containing 1,1,3-triphenylindene did not lead to detectible amounts of rearrangement product. Thus, indene **22** did not result from electron transfer induced rearrangement of **21**. If the radical anion of **21** is formed photochemically, its lifetime is too short to allow rearrangement, a fact which is supported by our results.

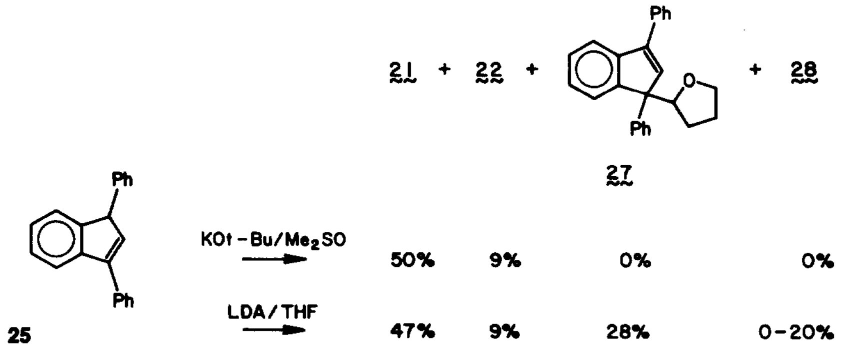
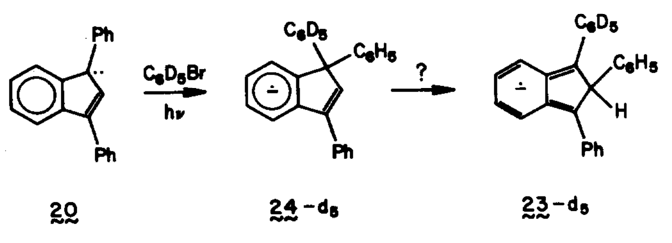


Fig. 7. Products of 1,3-diphenylindene arylation.



(11)

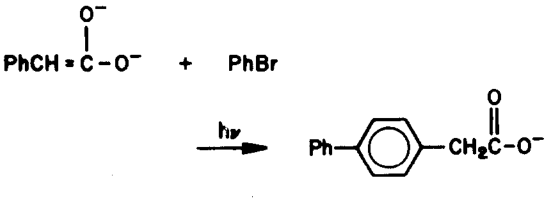
Table 1. Products of photoarylation of 1,3-diphenylindenyl anion (20)

Conc. 20	PhBr (equiv.)	Product Ratio (21/22)	Total Products (relative)
0.014 M	0.5	5.5	1.0
0.014 M	1.0	5.0	2.0
0.014 M	2.0	4.8	3.1
0.014 M	4.0	5.4	3.7
0.014 M	6.0	5.1	3.9

DISCUSSION

Kinetics vs thermodynamic control in free radical arylations

Clearly for 1,3-diphenylindenyl anion, regioselectivity is dominated by the influence of site basicity. This effect is in accord with our previous observations[9a] and is reminiscent of the preference for protonation at C-3 rather than C-1 in the cyclohexadienyl anion, despite the thermodynamic stability of the product derived from the latter. A rather intriguing further example of abnormal regiochemistry is due to Wolfe and Wong,[12] who observed facile para phenylation of phenylacetate dianion under photostimulation in the presence of bromobenzene, but no detectible α-phenylation (eqn 12). Again, we attribute these results to arylation at the site of greatest electron density (and highest kinetic basicity). These results are also in accord with the ready phenylation of the dianion of pentane-2,4-dione at C-1 but not at C-3.



Regioselectivity in ambident carbanions containing heteroatoms is somewhat more problematic. Reversibility may indeed play a role in selectivity for nitrocarbanions. However, the thermodynamics of such reactions requires loss of a very stable radical such as the p-nitrobenzyl radical. In other cases where regiochemical control is equally evident, loss of a radical such as phenyl radical would be energetically prohibitive. Thus the role of basicity in controlling selectivity in radical-anion mediated substitutions has much more general applicability than reversibility or thermodynamic arguments, and may also be the dominant feature even where reversibility is permitted.

Failure of reaction of certain nucleophiles

Any mechanistic rationale for the $S_{RN}1$ reaction must account for the failure of certain carbanions to undergo substitutions. We have previously suggested that certain carbanions, e.g. the enolate derived from pentane-2,4-dione, may not be competitive substrates for radical addition if the stability is too high, i.e. the basicity too low. However, strongly basic carbanions also fail to undergo substitution. Chief among these are carbanions derived from sulfur stabilized molecules such as 1,3-dithiane.[5b] We have shown that the overall energetics of free radical addition to negative ions may be estimated through the use of a thermochemical cycle. Hence, the energy released by this reaction may be arrived at by considering the process to involve protonation, exchange of proton for alkyl or aryl residue, and reduction of the resulting neutral. The energies of protonation are obtained from pK_a data, the alkyl exchange from heats of formation data, and the reduction from electrochemical data. An estimate for the overall thermodynamics of the reaction, then, is as follows:

$$\Delta G(S_{RN}1) = -2.3\,RTpK_a + \Delta\Delta G_f(R^{\cdot}) + n\mathcal{F}\mathcal{E}_{1/2}(H^+/H_2),$$

where pK_a is the acidity of the conjugate acid of the carbanion, $\Delta\Delta G_f$ is the difference of standard free energies of formation for the protonated and alkylated (or arylated) neutral minus free energy of formation of the radical, and $\mathcal{E}_{1/2}$ is the reduction potential of the product relative to the hydrogen electrode. $\Delta\Delta G_f$ for methyl has a value of 33–36 kcal/mol,[13] whereas $\Delta\Delta G_f$ for phenyl has the value 45–48 kcal/mol. Thus arylation is a slightly more favorable process than alkylation by *ca.* 12 kcal. This estimate provides a ceiling on the exothermicity of the reaction, since steric effects will tend to add a destabilizing term. In any event, the important result is that while the pK_a term dominates the kinetics of the reaction, the reduction potential dominates the overall thermodynamics. Thus if the radical anion being formed is of sufficiently low oxidation potential, reaction becomes energetically prohibitive, and poor radical anions such as dithiane radical anions fail to serve as intermediates in $S_{RN}{}^1$ reactions.

Summary. Photoinduced electron transfer reactions of carbanions continue to provide a rich variety of chemistry not readily accessible by ground state techniques. In particular, the generation of radicals under highly reducing homogeneous steady-state conditions allows a study of their reactivity without complicating side effects. Moreover, unlike dissolving metals, photochemically excited carbanions induce electron transfer in an ultimately reversible fashion, avoiding over reduction. An example is diphenyl sulfoxide, which undergoes facile photoreduction by carbanions to give phenyl radicals, although such a process is not observed on alkali metal surfaces.

The relative simplicity of the mechanistic pathways followed by resonance-stabilized carbanions upon excitation allows a ready differentiation between the effects of basicity and product stability upon rates of reaction of radicals with carbanions. We have found that basicity is the dominant constraint in photoarylations and photoalkylations of resonance-stabilized carbanions, and we see no evidence in work with other types of carbanions that would be in contradiction to this hypothesis.

An interesting question is the effect of *nucleophilicity* rather than basicity on the reaction outcome. To be sure, the ordering of reactivity in terms of basicity may instead reflect the corresponding ordering of nucleophilicity. More intriguing, and perhaps more likely, is the possibility that the difference between basicity and nucleophilicity may vanish for the reaction of nucleophiles with radicals. That is, differences between nucleophilicity and basicity are generally the result of polarization of charge in the transition state. Since there is no such polarization for the reaction with a radical, basicity and nucleophilicity may be indistinguishable.

EXPERIMENTAL

Materials. Dimethyl sulfoxide was purified following the procedure of Bordwell[14] and stored over moledular sieves under argon. Tetrahydrofuran was dried by distilling from a soln of sodium benzophenone ketyl and collected under argon. Diisopropylamine (Aldrich) was dried by reflux over calcium hydride and collected just prior to use. n-BuLi (1.6 M in hexane) was obtained from Aldrich Chemical Company. Potassium t-butoxide (Aldrich) was used from a freshly opened can without further purification.

1,3-Diphenylindene was prepared following two methods: that of Ziegler[15] and that developed in our laboratories.[16] Recrystallization from AcOH gave off-white prisms, m.p. 68–9° (lit.[15] m.p. 69–70°). 1,1,3-Triphenylindene, m.p. 136–7° and 1,2,3-triphenylindene, m.p. 130–1° were synthesized according to literature methods.[17]

Solutions of potassium t-butoxide in DMSO were prepared by syringing 20 ml dry Me_2SO into a degassed flask containing 112 mg (1.00 mmol) of potassium t-butoxide under argon.

Lithium diisopropylamide (LDA) was made by adding n-BuLi (2 ml, 3.2 mmol) to a 18 ml THF soln containing 0.5 ml (3.2 mmol) diisopropylamine at 0° under argon. The soln was allowed to equilibrate for at least 30 min prior to use.

Analyses. Gas chromatographic analysis was performed on a Varian 3700 gas chromatograph using a column of 3% OV-101 on Partisorb. NMR spectra were recorded on a Varian EM-390 spectrometer and are reported in δ units. Mass spectra were taken on a Hitachi Perkin–Elmer RMU-7 double focusing mass spectrometer. M.ps were taken on a hot-stage apparatus and are uncalibrated.

Manipulations. Apparatus and non-volatile materials were degassed repeatedly by evacuating and purging 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 using an Ace-Burlitch inert atmosphere system.

Irradiations. Irradiations were carried out using a Hanovia 450-W Lamp surrounded by a 0.1 M K_2CrO_4 soln in a pH 10 buffered medium which filtered all light below 450 mm. The solns were irradiated in 50 ml cylindrical pyrex vessels equipped with 3-way stopcocks and argon atmospheres.

Irradiation of 1,3-*diphenylindenylpotassium in* Me_2SO. 1,3-Diphenylindenyl anion was generated by treatment of the corresponding indene (268 mg, 1 mmol) in 40 ml Me_2SO with a 5% excess soln of BuOK in DMSO and photolyzed in the presence of bromobenzene (0.2 ml, ~2.0 mmol). Irradiation of the anion was monitored by gas chromatography to about 50% conversion (6–8 hr). Longer irradiation decreased the proportion of 1,2,3-triphenylindene formed. The reaction was quenched with water and extracted several times with CH_2Cl_2. The combined CH_2Cl_2 layer was dried and the crude material obtained after concentration *in vaco* was separated by preparative tlc (silica gel, E. Merck GF-254) using hexane as eluent. This yielded 86 mg (50%) of 1,1,3-triphenylindene and 15 mg (9%) of 1,2,3-triphenylindene. The products were identified by comparing the NMR and GC retention times with the independently synthesized samples. The percentages of the products reported are based on recovered starting material (130 mg).

Irradiation of 1,3-*diphenylindenyllithium in THF.* 1,3-Diphenylindenyl anion was prepared by treatment of 1,3-diphenylindene (268 mg, 1.00 mmol) in 50 ml dry THF with an equimolar amount of freshly prepared LDA at 0° and was allowed to equilibrate for 30 min at room temp. Bromobenzene (0.2 ml, 2 mmol) was added, and the soln was irradiated for 6–8 hr and quenched with water, the solvent removed *in vacuo*, and the residue taken up in ether-water mixture. The amine was extracted with dil HCl. Separation of the ether fraction by drying and concentrating *in vacuo* gave a brown residue. Preparative tlc (silica gel) yielded 80 mg (47%) of 1,13-triphenylindene, 18 mg (9%) of 1,2,3-triphenylindene and a third product (48 mg, 28%) which proved to be a diastereomeric mixture of 1-(2-tetrahydrofuryl)-1,3-diphenylindenes by NMR ($CDCl_3$): δ 1.2–1.7 (m, 4 H), 3.7–3.85 (m, 2 H), 4.75–5.05 (m, 1 H), 6.5 (S, H), 6.7 (S, H) and 7.15–7.7 (m, 14 H). Mass spectra of the compound had major peaks at 338, 267, 154 and 71. When larger than equivalent amounts of base (LDA) were employed, a new colorless crystalline product m.p. 160–3° was obtained. This product retained olefinic (6.8 δ) and allylic (5.4 δ) NMR resonances and had molecular ion 344.

Irradiation of 1,3-*diphenylindenyl anion with* d_5-*bromobenzene in* Me_2SO. To a soln of 1,3-diphenylindenyl anion made from 242 · mg (0.900 mmol) of 1,3-diphenylindene 10.0 ml (1.0 mmol) of 0.1 M t-BuOK in DMSO and 40 ml DMSO was added 0.18 ml (~2 mol) of d_5-bromobenzene. The soln was irradiated for 8 hr and quenched with water. The mixture was extracted several times with CH_2Cl_2 and the combined mixture dried and concentrated. The residue was purified by preparative silica gel tlc using hexane as eluent. 1,1,3-Triphenylindene-d_5 (45% yield) was pure by GC and tlc. 1,2,3-Triphenylindene-d_5 (15 mg, 9%) containing impurities was subjected to the same purification technique once more to yield a pure sample of 1,2,3-triphenylindene-d_5. The NMR or the compound was identical to that of undeuterated 1,2,3-triphenylindene except the peak at 7.05 had disappeared. The mass spectrum of the 1,2,3-triphenylindene-d_5 had major peaks at 349 (100%), 272 (67%), 268 (65%), 267 (33%), 265 (20%), 163 (20%) and 84 (75%).

Quenching reaction of 1,3-*diphenylindenyl anion with di-t-butyl nitroxide* (*DBN*). Three 15 ml photolyzing tubes (marked 1, 2 and 3) containing 1,3-diphenylindene (0.167 mmol) in each were degassed and kept under argon. 12 ML DMSO was introduced into each tube, followed by 1.0 ml of 0.17 M t-BuOK in DMSO. The anion was allowed to equilibrate for 30 min. DBN was introduced into tube 2 (24 mg, 0.167 mmol) and tube 3 (75 mg, 0.5 mmol). No DBN was added to tube 1. Equiv. amounts (0.167 mmol) of bromobenzene were added to each tube. The tubes were placed in a merry-go-round so as to ensure uniform light capture. The solns were irradiated for 2 hr and an aliquot (1 ml) was withdrawn from each tube and quenched. GC showed appreciable product formation in tube 1 and some in tube 2 but none in tube 3 within the limits of our GC detection system (< 0.1%). The irradiation was carried out for a total of 10 hr and the reactions quenched. The products were analyzed by GC and compared to the products from tube 1 containing no inhibitor. The amount of product formation in tubes 2 and 3, respectively, was 67% and 45% of the amount produced in the absence of DBN (tube 1).

Bromobenzene concentration studies. Solns of 0.014 M 1,3-diphenylindenyl anion were generated from equimolar amounts (0.17 mmol) of 1,3-diphenylindene, a 5% excess of potassium t-butoxide in DMOS and 12 ml DMSO in six separate 50 ml photolyzing tubes. After the anion had equilibrated for 30 min one-half, one, two, four, six and eight equivs of bromobenzene (relative to 1,3-diphenylindene) were introduced into the tubes. The soluns were irradiated in the merry-go-round with 0.1 M K_2CrO_4 filter for 20 hr and quenched with equal amounts (0.5 ml) of water. The ratio of formation of 1,1,3-triphenylindene to 1,2,3-triphenylindene was determined by gas chromatography calibrated with known mixtures. Results are presented in tabular form in Table 1. Relative product formation is also shown in that table.

Reaction of 1,1,3-*triphenylindene with sodium naphthalenide.* Sodium naphthalenide was generated in a 150 ml Schlenck tube from 0.3 g Na (13 mmol), 1.6 g naphthalene (12.5 mmol) in 40 ml freshly distilled THF under argon. The intense green naphthalene radical anion was formed within 6–8 hr. The sodium naphthalenide (0.1 mmol, 0.4 ml) was directly added under argon into a 25 ml three-neck round-bottomed flask containing 18 mg (0.05 mmol) of 1,13-triphenylindene in 3 ml dry THF and a stirring bar. The soln turned reddish-brown immediately; after 45 min of stirring at room temp it became light yellow. The reaction was quenched after 3 hr and the products analyzed by gas chromatography which showed 9 : 1 ratio of 1,2,3-triphenylindane to 1,2,3-triphenylindene. The product 1,2,3-triphenylindane was characterized by comparing its NMR spectrum with the reported [10a] chemical shifts.

Irradiation of 1,3-*diphenylindenyl anion in the presence of* 1,1,3-*triphenylindene in* Me_2SO. 1,3-Diphenylindenyl anion was made from 1,3-diphenylindene (27 mg, 0.10 mmol), 1.0 ml of a 0.10 M soln of t-BuOK in DMSO and 3.0 ml DMSO in a 15 ml photolyzing tube. The anion was allowed to equilibrate for 30 min, then 1,1,3-triphenylindene (6.0 mg, 0.02 mmol) in 2.0 ml DMSO was added to the tube. The soln was irradiated for 10 hr with the K_2CrO_4 filter soln. Gas chromatographic analysis of the quenched mixture showed no detectible amount of 1,2,3-triphenylindene.

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[13] The free energy change for this process can be most conveniently estimated by considering the exchange process

$$R.' + R'H \leftrightarrows R' + H.' \leftrightarrows RH + 1/2H_2$$

The enthalpy change for this reaction may be calculated by considering the difference in bond energies for a carbon-methyl bond (*ca.* 88 kcal) and for a C–H bond (104 kcal) and subtracting from the H–H bond energy (1/2 of 104). The corresponding difference in bond energies for C-phenyl (100 kcal) and C–H is only 4 kcal. Thus the enthalphy change for Me is 36 kcal and for phenyl is 48 kcal. These must be corrected to free energy changes by considering the entropy change for the honologation as well, which we estimate from thermodynamic data to contribute 3 kcal to the free energy.

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