filtered, and concentrated to give 4.76 g (51% overall yield) of 5-phenylvaleraldehyde (90–95% pure by vpc and nmr).[11]

Further studies are currently in progress to evaluate fully the potential of this synthetic method for obtaining a wide variety of aldehydes including those possessing additional functional groups.

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[11] All final products gave satisfactory mass, ir, nmr, and elemental analyses.

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Entrance onto Potential Energy Surfaces of Photochemical Reactions without Light. The Type B Reaction. Mechanistic Organic Photochemistry. LXVI[1]

Sir:

In 1961 we proposed mechanisms for the types A and B rearrangements in dienone photochemistry.[2] More recently we described the generation without light of zwitterionic intermediates now commonly accepted in the mechanism of the type A reaction.[3]

Presently we report generation without light of the zwitterion proposed[2] for the type B photochemical rearrangement in which 6,6-disubstituted bicyclo[3.1.0]hex-3-en-2-ones afford 2,3- and 3,4-disubstituted phenolic products and their tautomers.[4] The present results are sufficiently convincing that complete confirmation of the intermediacy of these zwitterions—for which considerable circumstantial evidence is available[2,5]—is now a reality.

We report: (1) generation of zwitterion B from the *tert*-butoxide treatment of 6-bromo-5,5-diphenylcyclohex-2-en-1-one (**1**),[6] (2) the observation of the same two phenols—2,3-diphenylphenol (**2**) and 3,4-diphenylphenol (**3**)—formed in the type B rearrangement of 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**4**),[2,7] (3) the identity of the ratios of these products from the dark and photochemical runs, and (4) the observation of identical solvent dependences of the dark and photochemical ratios of the two phenols **2** and **3**.

6-Bromo-5,5-diphenylcyclohex-2-en-1-one (**1**), mp 166°, was synthesized by pyrrolidone tribromide bromination of 5,5-diphenylcyclohex-2-en-1-one (**5**), mp 112°. The latter was obtained by bromination–dehydrobromination of 3,3-diphenylcyclohexanone (**6**), mp 115°. This ketone resulted from hydroboration of 4,4-diphenylcyclohexene (**7**), mp 66.5°, using an oxidative work-up and followed by a Jones oxidation. Finally, the diphenyl olefin **7** could be obtained by Wolff–Kishner reduction of 4,4-diphenylcyclohexenone.

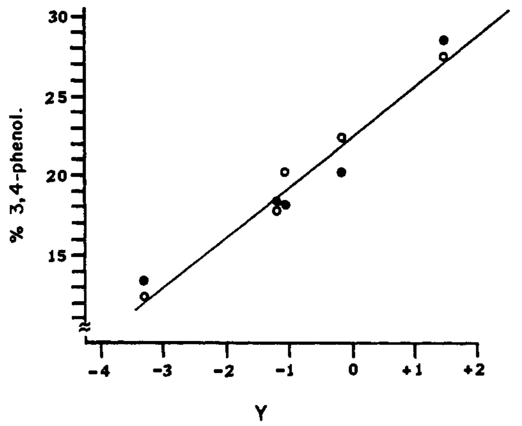

Figure 1. Plot of per cent 3,4-diphenylphenol obtained in dark and photochemical runs *vs.* *Y* values: ●, photochemical; ○, dark.

Potassium *tert*-butoxide treatment of 6-bromo-5,5-diphenylcyclohex-2-en-1-one (**1**) in *tert*-butyl alcohol at room temperature for 6 hr gave in 86% yield a mixture of 2,3-diphenylphenol (**2**) and 3,4-diphenylphenol (**3**). The ratio of phenols was analyzed by three methods: vpc on 5% SE-30 on Varaport 30, quantitative infrared analysis, and chromatographic separation and isolation.

These are the same two phenols obtained from the photolysis of 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**4**).[2,7] Strikingly, the ratio of the phenols obtained in the base-catalyzed treatment of bromo ketone **1** was identical with that from the photolysis.

Furthermore, the photolysis in different solvents was found to give a distribution of phenols which was a smooth, nearly linear function of solvent polarity as measured by *Y* value[8] as shown in Figure 1 and in Table I. It was found that the percentage of 3,4-diphenylphenol (**3**) increased with solvent polarity.

Table I. Distribution[a] of Phenols from Zwitterion

Solvent	Photochemical 3,4-diphenylphenol, %	Dark reaction 3,4-diphenylphenol, %	*Y*
tert-Butyl alcohol[b]	13.6 ± 2.5[e]	12.4 ± 1.0[d]	−3.3[f]
95% ethanol–water[c]	18.4 ± 1.0[d]	17.6 ± 1.0[d]	−1.3[f]
80% *tert*-butyl alcohol–water[c]	18.0 ± 2.5[e]	20.4 ± 2.5[e]	−1.1[g]
73% dioxane–water[c]	20.2 ± 2.5[e]	22.6 ± 2.5[e]	−0.2[g]
50% dioxane–water[c]	28.5 ± 1.0[d]	27.5 ± 1.0[d]	+1.4[f]

[a] Tabulating the percentage of 3,4-diphenylphenol in the mixture of 2,3-diphenylphenol and 3,4-diphenylphenol. [b] Potassium *tert*-butoxide used as a base. [c] Potassium hydroxide used as a base. [d] Vpc analysis. [e] Quantitative infrared analysis—vpc analysis not performed. [f] Values of Winstein.[8] [g] Values not reported in the literature—obtained using the observation of W. H. Cropper, F. Spieth, and A. R. Olson (*J. Amer. Chem. Soc.*, **76**, 6248 (1954)) that the plot of *Y* *vs.* per cent water is linear in the region of low percentages of water.

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(1) For paper LXV of the series, note H. E. Zimmerman and D. S. Crumrine, *J. Amer. Chem. Soc.*, **94**, 498 (1972).

(2) (a) H. E. Zimmerman, 17th National Organic Chemistry Symposium, Bloomington, Ind., June 1961, Abstracts, p 31; (b) H. E. Zimmerman and D. I. Schuster, *J. Amer. Chem. Soc.*, **83**, 4486 (1961); (c) *ibid.*, **84**, 4527 (1962).

(3) H. E. Zimmerman and D. S. Crumrine, *ibid.*, **90**, 5612 (1968).

(4) (a) H. E. Zimmerman, *Advan. Photochem.*, **1**, 183 (1963); (b) H. E. Zimmerman, *Angew. Chem., Int. Ed. Engl.*, **8**, 1 (1969).

(5) H. E. Zimmerman and J. O. Grunewald, *J. Amer. Chem. Soc.*, **89**, 5163 (1967).

(6) Synthetic details will be given in our full paper. All compounds analyzed satisfactorily.

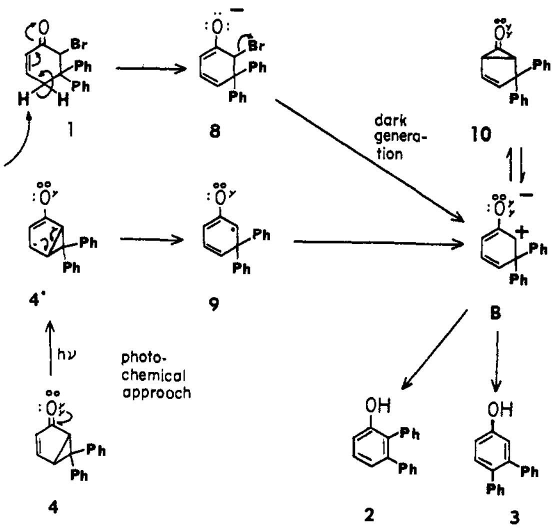
(7) H. E. Zimmerman, R. Keese, J. Nasielski, and J. S. Swenton, *J. Amer. Chem. Soc.*, **88**, 4895 (1966).

(8) (a) E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, **70**, 846 (1948); (b) S. Winstein, E. Grunwald, and H. W. Jones, *ibid.*, **73**, 2700 (1951); (c) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956).

The most striking feature was the identical points obtained from the dark and photochemical runs. Thus, not only were the same two products obtained from the base treatment of bromo ketone **1** as in the photochemical approach, but their distribution and solvent dependency of their distribution proved independent of whether light or base was employed. This provides convincing evidence that there is a precursor common to the two reactions, photochemical and dark.

Actually, bromo ketone **1** had been designed to generate zwitterion B in the absence of light. It was reasoned that enolate **8** obtained in base would be a doubly allylic bromide which would solvolyze with facility to zwitterion B. This mechanism, along with the photochemical approach, is depicted in Chart I.

Chart I. Generation and Rearrangement of Zwitterion B in Dark and Photochemical Approaches



Three additional points are of interest. First, the collapse of zwitterion B to bicyclic enone **4** is forbidden electronically and no **4** is observed from the dark generation of zwitterion B. This establishes that the relatively low efficiency of the photochemical process to give phenols **2** and **3** from bicyclic enone **4** does not derive from reversion of zwitterion B to photochemical reactant. This point could not be established in our earlier photochemical studies. Secondly, although cyclopropanone **10** has been reported as being formed at low temperatures by Chapman[9] from the photolysis of **4**, and despite the possibility of its being formed from the dark reaction presently, it does not account for the cationic rearrangement observed. Nevertheless, it may be present in equilibrium with zwitterion B and such equilibration is electronically allowed. Thirdly, in providing evidence for zwitterion B as an intermediate, the independent generation of B in the dark argues against rearrangement of an electronically excited species as **9** prior to loss of electronic excitation. This agrees with our previously observed migratory aptitude study in which phenyl migrated in preference to cyanophenyl in the type B process.[5] Thus we have defined the stage of the reaction by which electronic relaxation occurs.

It is seen that dark generation of species occurring on surfaces normally accessible photochemically promises to provide an independent means of studying photochemical mechanisms.

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(9) O. L. Chapman, 3rd International IUPAC Symposium on Photochemistry, St. Moritz, July 1971.

Temperature-Dependent Electron Delocalization in Diphenyldimethylsilane

Sir:

As part of our continuing studies on electron delocalization in silyl compounds,[1] we have investigated compounds of the form $[\mathrm{Ph}(\mathrm{SiR_2})_n\mathrm{Ph}]\cdot^-$, (R = H = Me; *n* = 1–3) by esr spectroscopy. In $[\mathrm{PhSiMe_2Ph}]\cdot^-$ we have observed what we believe is the first reported example of reversible, temperature-dependent electron delocalization. At low temperatures ($T < -70°$), the unpaired electron in this radical anion is localized on one phenyl ring; at higher temperatures, it appears to be delocalized equally over both phenyl moieties.

Figure 1 shows the esr spectrum of $[\mathrm{PhSiMe_2Ph}]\cdot^-$ at $-80°$. This radical anion could be generated either chemically (with Na–K alloy in 2:1 2-methyltetrahydrofuran–1,2-dimethoxyethane) or electrolytically (in THF, with tetra-*n*-butylammonium perchlorate as the supporting electrolyte). The hyperfine pattern ($2 \times 3 \times 3$) clearly shows the unpaired electron to be localized on one phenyl ring. As first shown by Carrington, *et al.*,[2] the coupling constants may be assigned as follows: $A_{\mathrm{H,p}} = 8.56$ G; $A_{\mathrm{H,o}} = 2.94$ G; $A_{\mathrm{H,m}} = 1.47$ G; $A_{\mathrm{H,SiMe}}$, not observed.

When the temperature of the sample was raised to $> -40°$, the spectrum shown in Figure 2 appeared. The hyperfine pattern is a triplet of quintets, consistent with electron delocalization over both phenyl rings. The triplet splitting is assigned to hyperfine splitting by the two equivalent para hydrogens ($A_{\mathrm{H,p}} = 4.25$ G), and the quintet to coupling with the four equivalent ortho hydrogens ($A_{\mathrm{H,o}} = 1.37$ G). Neither silyl methyl nor meta hydrogen interaction is apparently observed. This high-temperature spectrum was not due to a decomposition product, since recooling the sample to $-80°$ restored the original spectrum.

Additional support for this interpretation of the temperature effect is given by the relation of the coupling constants of the ortho and para protons for the high- and low-temperature species. The values for both sets of protons in the high-temperature spectrum are approximately one-half those in the low-temperature spectrum, consistent with the decrease by one-half of π-electron density at each site upon delocalization.

Makarov, Kazakova, and Syrkin[3] found the unpaired electron to be localized on one ring at $-70°$, but reported decomposition of the parent anion radical to $[\mathrm{PhSiMe_2PhSiMe_2Ph}]\cdot^-$ and $[\mathrm{biphenyl}]\cdot^-$ as the temperature was raised to $+20°$. It is not surprising

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(1) G. R. Husk and R. West, *J. Amer. Chem. Soc.*, **87**, 3993 (1965); E. Carberry, R. West, and G. E. Glass, *ibid.*, **91**, 5446 (1969).

(2) J. A. Bedford, J. R. Bolton, A. Carrington, and R. H. Prince, *Trans. Faraday Soc.*, **59**, 53 (1963).

(3) I. G. Makarov, V. M. Kazakova, and Ya. K. Syrkin, *J. Struct. Chem.*, **8**, 137 (1966).