

important to consider other features besides an empirical "hardness" scale based purely upon thermochemical methods,⁸ where the order necessarily refers to alkyl cations with the same geometry of the alkyl moiety in their neutral precursors. A more general warning against thermochemical approaches to "hardness" scales for charged electrophiles stems from the observation that the chemical "hardness" concept is often used to weigh electron mixing in the transition state for Lewis acid–base reactions and

its effect on the relevant energy level. Thus, one should not be surprised if the alkyl cation "hardness" scale derived from the present gas-phase kinetic investigation does not match the one empirically inferred from thermochemical considerations.

Registry No. 1, 109-97-7; 2, 96-54-8; 3, 110-00-9; 4, 110-02-1; C₂H₅⁺, 14936-94-8; CH₃⁺, 14531-53-4; NMe₃, 75-50-3; *i*-C₃H₇⁺, 19252-53-0; *t*-C₄H₉⁺, 14804-25-2; 2-ethylpyrrole, 1551-06-0; 3-ethylpyrrole, 1551-16-2; *N*-ethylpyrrole, 617-92-5; 2-ethyl-*N*-methylpyrrole, 24037-61-4; 3-ethyl-*N*-methylpyrrole, 53871-25-3; 2-ethylfuran, 3208-16-0; 3-ethylfuran, 67363-95-5; 2-ethylthiophene, 872-55-9; 3-ethylthiophene, 1795-01-3.

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Radical Ions in Photochemistry.¹ Carbon–Carbon Bond Cleavage of Radical Cations in Solution: Theory and Application

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Abstract: The cleavage of radical cations of two series of alkanes, 1,1,2-triaryl- and 1,1,2,2-tetraaryllkanes, generated by photoinduced single electron transfer in acetonitrile–methanol, occurs with formation of radical and carbocation fragments. The radical cations of some unsymmetrically substituted alkanes cleave to give all four of the possible products, two hydrocarbons emanating from the radicals and two methyl ethers from the carbocations, in proportion to the oxidation potentials of the two possible radical fragments. There is an excellent linear correlation between the logarithm of the observed ratio of products and that calculated from the reported electrochemically determined oxidation potentials ($r = 0.998$, 5 points). The proportionality constant (1.27) for this relationship is close to unity which indicates that the product ratio is determined by the relative rates of cleavage in the two possible modes or by equilibration of the radicals and carbocations before separation of the geminate radical carbocation pair and not by equilibration upon reencounter of freely solvated radical and carbocation fragments. The effect of temperature on the relative oxidation potentials of the radicals studied is small and can be neglected when radicals of the same order (i.e., both secondary or both tertiary) and of similar size are compared. The ratio of products obtained upon cleavage of the radical cation at 25 °C can be used to determine standard oxidation potentials of radicals. The oxidation potential of the diphenylmethyl radical (0.350 V vs SCE) has been accepted as the primary standard and the (4-methylphenyl)phenylmethyl (0.265 V) and bis(4-methylphenyl)methyl (0.188 V) radicals are established as secondary standards against which the oxidation potentials of other radicals can be measured. Oxidation potentials of several 4-substituted cumyl radicals have been determined by this photochemical method. There is a good ($r = 0.987$, 5 points) linear correlation between the measured oxidation potentials and the σ^+ substituent constants. The reaction constant is appropriately negative and large ($\rho = -6$).

Several years ago we reported that irradiation of an acetonitrile–methanol (3:1) solution of methyl 2,2-diphenylethyl ether (1) and 1,4-dicyanobenzene (2) led to the formation of diphenylmethane (3) and the dimethyl acetal of formaldehyde (4) in high yield (reaction 1 in Scheme I).² Key steps in the proposed mechanism (Scheme II) involve formation of the radical cation of the ether by single electron transfer to the singlet excited state of 2, followed by carbon–carbon bond cleavage of the resulting radical cation. No methyl diphenylmethyl ether (5) was detected. Apparently cleavage of the radical cation of 1 occurs with the exclusive formation of the diphenylmethyl radical and the α -oxycarbocation. The explanation offered for this regioselectivity was that cleavage occurred to give the carbocation of that radical fragment which had the lower oxidation potential. At the time the oxidation potential of the α -oxymethyl radical was not known. The value subsequently reported is compatible with this explanation. The oxidation potential of the diphenylmethyl radical (0.35 V vs SCE, all of the electrochemical potentials mentioned in this paper are relative to the saturated calomel electrode) is 0.6 V

higher than that of the α -oxymethyl radical.³

There have been several recent reports which deal with this type of reaction, and the salient features of the originally proposed mechanism remain intact.^{4,5} There are however several important points that require further clarification, and this paper deals primarily with two of them. (1) The reaction is *not* general—on what basis can reactivity be predicted? (2) Only two products are obtained upon cleavage of some radical cations, while all four

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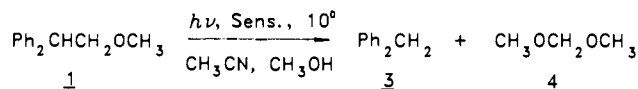
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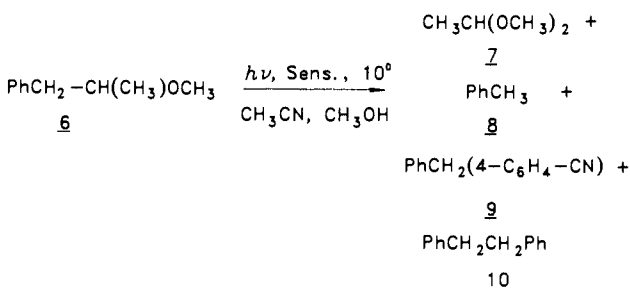
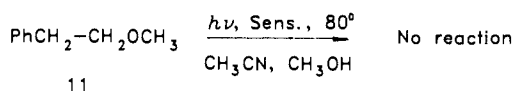
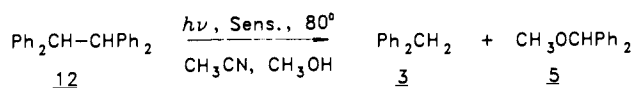
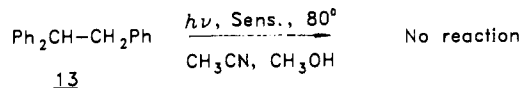
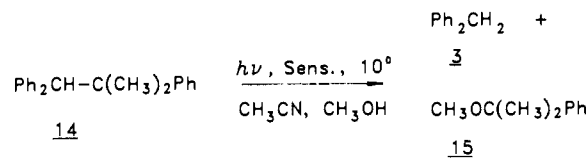
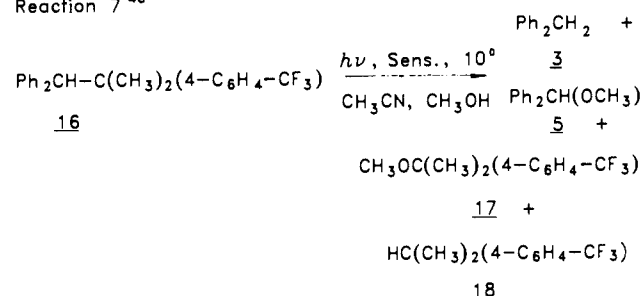
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Scheme I

Reaction 1²

Sens. = 1,4-Dicyanobenzene (2)

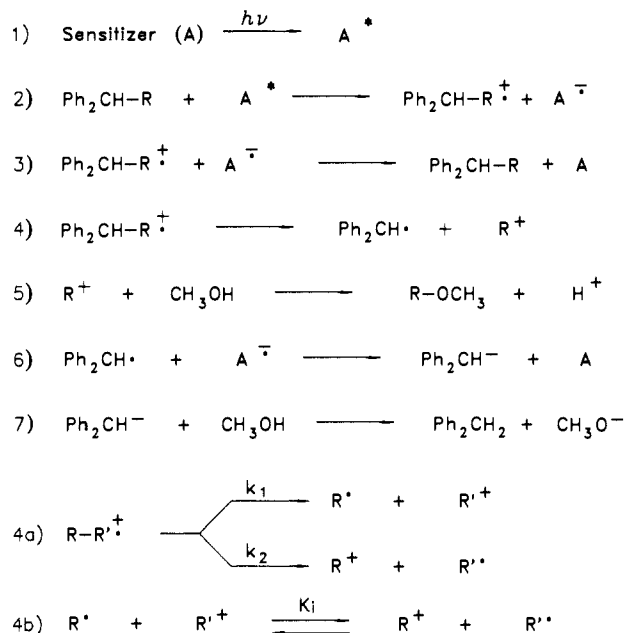
Reaction 2⁴⁰Reaction 3⁴⁰Reaction 4^{4c}Reaction 5⁴⁰Reaction 6^{4d}Reaction 7^{4d}

possible products result from some others—what factors determine which fragment will ultimately be incorporated into the hydrocarbon and which will be incorporated into the ether, and can the ratio of products be predicted?

A few examples of the reactivity of similar compounds, identifying some that do and some that do not cleave upon irradiation under standard conditions for single electron transfer (acetonitrile-methanol as solvent, temperature held at 10 °C, with 2 as an electron accepting photosensitizer) will introduce the first problem.

While the radical cation of methyl 2-(1-phenylpropyl) ether (6) cleaves in the expected way (reaction 2 in Scheme I), methyl

Scheme II. The Mechanism for the Photosensitized (Electron Transfer) Carbon-Carbon Bond Cleavage



2-phenylethyl ether (11) is stable to irradiation under these conditions (reaction 3 in Scheme I).^{4a} The reactivity of the radical cation of 1,1,2-tetraphenylethane (12) is temperature dependent; no cleavage occurs when the irradiation is carried out at 10 °C, but at 80 °C the cleavage reaction is relatively efficient (reaction 4 in Scheme I).^{4c} In contrast, 1,1,2-triphenylethane (13) is stable to irradiation even at the higher temperature (reaction 5 in Scheme I).^{4a} Reactivity is restored upon the addition of two methyl groups to that fragment which will ultimately become the carbocation; the radical cation of 1,1,2-triphenyl-2-methylpropane (14) cleaves when the irradiation is carried out at 10 °C (reaction 6 in Scheme I).^{4d} It is apparent, even from the few examples reviewed here, that the cleavage reaction depends upon the bond dissociation energy of the carbon-carbon bond in the radical cation and that cleavage can be thermally activated. Study of the relative efficiency of the cleavage as a function of temperature (reaction 4 in Scheme I)^{4c} and consideration of thermochemical data have set the threshold for the activation energy (10–15 kcal mol⁻¹), above which cleavage will not be observed under these reaction conditions.^{4a,c} The problem remains: bond dissociation energies of radical cations in solution are largely unknown, except for some examples that have been estimated from thermochemical data.^{4,6} It is therefore generally not yet possible to anticipate when this cleavage reaction will occur. We will provide several more examples of the cleavage reaction and will discuss the application of a thermochemical cycle for predicting reactivity.

An explanation for the regioselectivity of the cleavage process was offered earlier following a study of the effect of substituents on the product ratio from the radical cations of some substituted 1,1,2-triphenyl-2-methylpropanes.^{4d} While cleavage of the radical cation of the parent 1,1,2-triphenyl-2-methylpropane (14) gave only two products, diphenylmethane (3) and cumyl methyl ether (15) (reaction 6 in Scheme I), the derivative bearing a 4-trifluoromethyl substituent on the cumyl moiety (16) gave an almost equal mixture of all four possible cleavage products (reaction 7 in Scheme I).^{4d} It was clear that the product ratio was dependent upon the redox properties of the two radical fragments. The oxidation potentials of the radicals were not known, so the extent and cause of the dependence could not be determined.

In this paper, a more rigorous evaluation of the regioselectivity of the cleavage process based upon the relative oxidation potentials of the two radical fragments is developed and new experimental

Table I. Product^a Composition After Cleavage of the Radical Cation of 1-(4-Methylphenyl)-1,2,2-triphenylethane (**19**)^b in Acetonitrile–Methanol (3:1) Solution

| temp (°C) | 3 | 32 | 5 | 33 | conv (%) | time (h) |
|-----------|----------|-----------|----------|-----------|----------|----------|
| 80 | 53.3 | 4.26 | 3.44 | 39.0 | 10 | 8.4 |
| 75 | 49.0 | 4.33 | 3.80 | 42.8 | 10 | 16.6 |
| 70 | 51.4 | 3.34 | 2.39 | 42.9 | 23 | 33.2 |
| 70 | 42.5 | 2.93 | 2.90 | 51.7 | 20 | 18.0 |
| 65 | 45.2 | 2.89 | 1.91 | 50.0 | 24 | 42.6 |
| 60 | 55.2 | 3.11 | 2.21 | 39.5 | 16 | 52.3 |
| 55 | 45.9 | 2.70 | 2.43 | 49.0 | 16 | 67.4 |
| 50 | 55.2 | 2.42 | 1.69 | 40.7 | 18 | 101.4 |
| 40 | 53.3 | 2.57 | 1.48 | 42.7 | 8 | 162.6 |

^aDiphenylmethane (**3**), (4-methylphenyl)phenylmethane (**32**), methyl diphenylmethyl ether (**5**), methyl (4-methylphenyl)phenylmethyl ether (**33**), (mol %). ^bInitial concentrations: **19**, 0.05 M; **2**, 0.02 M.

evidence is provided which supports the proposed theory. The newly defined quantitative relationship between the oxidation potentials of the radical fragments, and the product ratio will then be applied to determine the relative oxidation potentials of some radicals that have not yet been studied by electrochemical methods.

Results

The compounds selected for study are shown in Chart I. These compose two series, one of the five tetraarylalkanes and the other the 12 triarylalkanes. All of these compounds were obtained by well-established procedures. 1,1,2,2-Tetra-phenylethane (**12**) and 1,1-bis(4-methylphenyl)-2,2-diphenylethane (**20**) were prepared by coupling benzhydryl chloride with 4,4'-dimethylbenzhydryl chloride by the Wurtz reaction. The resulting mixture of the unsymmetric cross-coupling product and the two symmetrically coupled products was separated by using preparative high pressure liquid chromatography (HPLC). When this procedure was applied to the synthesis of 1-(4-methylphenyl)-1,2,2-triphenylethane (**19**) and 1,1,2-tris(4-methylphenyl)-2-phenylethane (**21**), separation of the resulting mixtures, which are made more complex by the presence of the diastereomers formed upon coupling of the (4-methylphenyl)phenylmethyl radical, was unsuccessful. These unsymmetric tetraarylethanes were therefore synthesized by an alternative longer but selective method outlined in Scheme III for the preparation of **21**. 1,1,2,2-Tetra-phenylpropane (**22**) was prepared by the reaction of the 1,1-diphenylethyl anion with benzhydryl chloride. The triarylalkanes were similarly prepared by the reaction of a diarylalkyl anion with a benzylic halide.

The major products obtained upon irradiation were isolated and fully characterized by direct comparison (gas chromatography with mass selective detection (GC/MS, retention time and mass spectrum) and ¹H NMR spectrum) with authentic material in the case of known compounds and by spectral techniques and combustion analysis when the compound had not been reported. Details are given in the Experimental Section.

The conditions of the irradiations were similar to those used in our previous study, so the results can be directly compared.⁴ Solutions of the arylalkane (0.05–0.10 M) and 1,4-dicyanobenzene (**2**) (0.02 M) in acetonitrile–methanol (3:1) were irradiated through Pyrex by using a medium-pressure mercury vapor lamp. Aliquots were taken for gas chromatographic analysis (GC/fid, capillary column, calibrated flame ionization detection) after low (<50%) conversion.

The reactions involving the tetraarylalkanes, particularly the cleavage of 1-(4-methylphenyl)-1,2,2-triphenylethane (**19**) and 1,1,2-tris(4-methylphenyl)-2-phenylethane (**21**), behaved "ideally". That is, competing reactions were insignificant, the material balance involving all four products (two hydrocarbons and two ethers) was good, and the ratios of products resulting from cleavage in both possible modes were internally consistent and accurately measured. The product ratios obtained upon cleavage of **19** and **21** were studied as a function of temperature. These results are summarized in Tables I and II. The cleavage of **21** was repeated several times at each temperature in order to determine the accuracy and reproducibility of the method. A summary of these

Table II. Product^a Composition After Cleavage of the Radical Cation of 1,1,2-Tris(4-methylphenyl)-2-phenylethane (**21**)^b in Acetonitrile–Methanol (3:1) Solution

| temp (°C) | 32 | 34 | 33 | 35 | conv (%) | time (h) |
|-----------|-----------|-----------|-----------|-----------|----------|----------|
| 80 | 46.1 | 3.72 | 3.56 | 46.6 | 22 | 5.5 |
| | 47.0 | 3.43 | 3.56 | 46.0 | 21 | 5.5 |
| | 45.4 | 3.50 | 3.21 | 47.9 | 14 | 5.1 |
| | 45.0 | 3.73 | 3.25 | 48.0 | 29 | 6.5 |
| 65 | 45.3 | 3.51 | 3.23 | 48.0 | 49 | 5.6 |
| | 49.9 | 3.54 | 2.97 | 43.6 | 44 | 5.6 |
| | 49.3 | 3.16 | 2.88 | 44.7 | 11 | 5.8 |
| | 47.4 | 3.32 | 2.72 | 46.6 | 12 | 5.8 |
| | 49.7 | 3.43 | 2.85 | 44.0 | 26 | 8.2 |
| 50 | 49.5 | 3.03 | 2.70 | 44.7 | 27 | 17.2 |
| | 48.4 | 2.99 | 2.79 | 45.8 | 29 | 17.2 |
| | 47.9 | 3.08 | 2.98 | 46.0 | 24 | 16.0 |
| | 48.6 | 3.00 | 2.70 | 45.7 | 19 | 16.0 |
| 35 | 50.5 | 2.53 | 2.43 | 44.5 | 19 | 16.0 |
| | 48.7 | 2.74 | 2.46 | 46.1 | 13 | 16.0 |
| | 50.6 | 2.64 | 2.43 | 44.3 | 18 | 16.0 |
| | 49.7 | 2.77 | 2.36 | 45.2 | 14 | 16.0 |
| 20 | 47.0 | 2.51 | 2.49 | 48.0 | 14 | 23.0 |
| | 49.5 | 2.32 | 2.14 | 46.0 | 9 | 23.0 |
| | 49.2 | 2.40 | 2.25 | 46.2 | 14 | 23.0 |
| | 48.1 | 2.34 | 2.28 | 47.3 | 14 | 23.0 |
| | 45.7 | 2.25 | 2.41 | 49.7 | 13 | 23.0 |

^a(4-Methylphenyl)phenylmethane (**32**), bis(4-methylphenyl)-methane (**34**), methyl (4-methylphenyl)phenylmethyl ether (**33**), methyl bis(4-methylphenyl)methyl ether (**35**), (mol %). ^bInitial concentrations: **21**, 0.05 M; **2**, 0.02 M.

Table III. The Ratio of Hydrocarbons (r_1) and Ethers (r_2), Formed upon Cleavage of the Radical Cation of 1,1,2-Tris(4-methylphenyl)-2-phenylethane (**21**), as a Function of Temperature

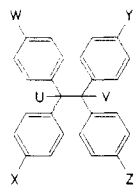
| temp (°C) | r_1^a | r_2^b | temp (°C) | r_1^a | r_2^b |
|-----------|------------|------------|-----------|------------|------------|
| 80 | 12.8 ± 0.7 | 13.9 ± 1.1 | 35 | 18.7 ± 1.0 | 18.6 ± 0.4 |
| 65 | 14.3 ± 1.0 | 15.5 ± 1.0 | 20 | 20.3 ± 0.9 | 20.5 ± 0.8 |
| 50 | 16.1 ± 0.3 | 16.3 ± 0.6 | | | |

^a r_1 = (4-methylphenyl)phenylmethane (**32**)/bis(4-methylphenyl)-methane (**34**). ^b r_2 = methyl bis(4-methylphenyl)methyl ether (**35**)/methyl (4-methylphenyl)phenylmethyl ether (**33**).

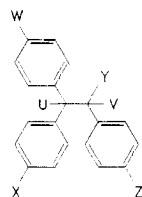
data is shown in Table III. The product ratios (e.g., **32/34** and **35/33** from **21**) are in good agreement and are temperature dependent.

Cleavage of the radical cation of 1,1-bis(4-methylphenyl)-2,2-diphenylethane (**20**) gave diphenylmethane (**3**) and methyl bis(4-methylphenyl)methyl ether (**35**) in good yield; less than 2% of bis(4-methylphenyl)methane (**34**) and methyl diphenylmethyl ether (**5**) were formed. This ratio of major to minor products was too large to be accurately determined; the ratio of integrated peak areas exceeded the dynamic range of the data acquisition system. The same problem was encountered during the study of 1,1,2,2-tetra-phenylpropane (**22**). This reaction was further complicated by the fact that **22** is thermally unstable; products resulting from homolytic cleavage (i.e., radical cross-coupling and disproportionation products) were formed by a dark reaction. Still, the approximate ratio of ethers can be used to indicate the dominant mode of cleavage of the radical cation. Methyl 1,1-diphenylethyl ether (**36**) was the major product (41%) observed upon cleavage of the radical cation of **22**, and only a trace (<1%) of methyl diphenylmethyl ether (**5**) was detected.

The cleavage of the triarylalkanes was studied under the same conditions and over the same temperature range as used for the tetraarylalkanes. The reaction mixtures were frequently more complex with these compounds; products in addition to the two hydrocarbons and ethers were obtained. An effort was made to isolate and identify all of the products, and the material balance generally was good (>90%), particularly when the irradiation was carried out at higher temperature (80 °C) and low conversion. Typical results, those from irradiation at 80 °C, are summarized in Table IV.

Chart I. The Compounds Studied Can Be Divided into Two Series, Tetraarylalkanes and Triarylalkanes

| Compound | No. | U | V | W | X | Y | Z |
|--|-----|---|-----------------|---|-----------------|-----------------|-----------------|
| 1,1,2,2-TetraPhenylethane | 12 | H | H | H | H | H | H |
| 1-(4-Methylphenyl)-1,2,2-triphenylethane | 19 | H | H | H | H | H | CH ₃ |
| 1,1-Bis(4-methylphenyl)-2,2-diphenylethane | 20 | H | H | H | H | CH ₃ | CH ₃ |
| 1,1,2-Tris(4-methylphenyl)-2-phenylethane | 21 | H | H | H | CH ₃ | CH ₃ | CH ₃ |
| 1,1,2,2-TetraPhenylpropane | 22 | H | CH ₃ | H | H | H | H |



| Compound | No. | U | V | W | X | Y | Z |
|--|-----|-----------------|-----------------|-----------------|-----------------|-----------------|------------------|
| 1,1,2-Triphenylethane | 13 | H | H | H | H | H | H |
| 1,1,2-Triphenylpropane | 23 | H | CH ₃ | H | H | H | H |
| 2-Methyl-1,1,2-triphenylpropane | 14 | H | CH ₃ | H | H | CH ₃ | H |
| 2-(4-Cyanophenyl)-2-methyl-1,1-diphenylpropane | 24 | H | CH ₃ | H | H | CH ₃ | CN |
| 2-(4-(Trifluoromethyl)phenyl)-2-methyl-1,1-diphenylpropane | 16 | H | CH ₃ | H | H | CH ₃ | CF ₃ |
| 2-(4-Methoxyphenyl)-2-methyl-1,1-diphenylpropane | 25 | H | CH ₃ | H | H | CH ₃ | OCH ₃ |
| 2-(4-Fluorophenyl)-2-methyl-1-(4-methylphenyl)-1-phenylpropane | 26 | H | CH ₃ | CH ₃ | H | CH ₃ | F |
| 2-(4-Fluorophenyl)-2-methyl-1,1-bis(4-methylphenyl)propane | 27 | H | CH ₃ | CH ₃ | CH ₃ | CH ₃ | F |
| 2,2,3-Triphenylbutane | 28 | CH ₃ | CH ₃ | H | H | H | H |
| 2-Methyl-1-(4-methylphenyl)-1,2-diphenylpropane | 29 | H | CH ₃ | CH ₃ | H | CH ₃ | H |
| 2-Methyl-1,1-bis(4-methylphenyl)-2-phenylpropane | 30 | H | CH ₃ | CH ₃ | CH ₃ | CH ₃ | H |
| 2-Methyl-1,1,2-tris(4-methylphenyl)-propane | 31 | H | CH ₃ | CH ₃ | CH ₃ | CH ₃ | CH ₃ |

Discussion

On What Basis Can Reactivity Be Predicted? The first step in the proposed mechanism for the cleavage reaction (Scheme II) is excitation of the electron-accepting sensitizer (A). The long wavelength absorption of 1,4-dicyanobenzene (**2**) extends beyond the absorption cutoff of the Pyrex filter (ca. 280 nm). The arylalkanes are transparent in this region. Dicyanobenzene (**2**) has a relatively long-lived first excited singlet state ($\tau = 9.7$ ns).²

Arylalkanes quench the fluorescence of **2** at the diffusion-controlled rate.² The mechanism for this quenching process (step 2 in Scheme II) is electron transfer. Substitution of the singlet energy and reduction potential of **2** (97.6 kcal mol⁻¹ and -1.66 V)² in the Weller equation (eq 1) indicates that the first excited singlet state of **2** is capable of oxidizing any donor with an oxidation potential <2.4 V at the diffusion-controlled rate 1.8×10^{10} M⁻¹ s⁻¹.⁷ The oxidation potentials of arylalkanes are well below this limit: arylalkane ($E_{1/2}^{ox}$ V vs SCE), 1,1,2,2-tetraPhenylethane (**12**) (2.01),^{4c} 1-(4-methylphenyl)-1,2,2-triphenylethane (**19**) (1.89), 1,1-bis(4-methylphenyl)-2,2-diphenylethane (**20**) (1.83), and 1,1,2-tris(4-methylphenyl)-2-phenylethane (**21**) (1.82). When the electron-transfer process is energetically favorable and when

the solvent is polar, as it is in these reactions, involvement of an exciplex is unlikely, and the result of step 2 (in Scheme II) is formation of the arylalkane radical cation-dicyanobenzene radical anion geminate pair.

$$\Delta G_{et} = F[E_{1/2}^{ox}(D) - E_{1/2}^{red}(A) - e/\epsilon\alpha] - E_{0,0}(A) \quad (1)$$

F is the Faraday constant, and the last term in the brackets takes into account the Coulombic attraction between the radical cation and the radical anion.

Step 3 in Scheme II is back electron transfer from the radical anion to the radical cation. This is the main competing process in every case and dominates when no cleavage is observed. The free energy change (ΔG) for this process, estimated from eq 2, is very exergonic (ca. 3.5 eV, >80 kcal mol⁻¹). This large energy gap slows the process, that is, the rate falls in the Marcus inverted region.⁸ The rate of solvent (acetonitrile) separation of several geminate radical-ion pairs, similar to those involved here, is ca. 5×10^8 s⁻¹.⁸ Back electron transfer may in fact be slower. The lifetime of the geminate radical-ion pair may be as long as 10^{-8} s which is long enough for the radical cation cleavage to occur within the pair.

$$\Delta G_{-et} = F(E_{1/2}^{red}(A) - E_{1/2}^{ox}(D)) \quad (2)$$

Step 4 in Scheme II represents the cleavage of the radical cation. The variation in reactivity of seemingly similar compounds has been explained in terms of the difference in rate of this crucial step in competition with deactivation by back electron transfer; compare, for example, reactions 2 and 3 and reactions 4 and 5 (in Scheme I). The temperature dependence of the reactivity of **12** has also been attributed to an activation barrier for the bond cleavage. When the logarithm of the relative efficiency of the cleavage of **12** (reaction 4 in Scheme I) was plotted as a function of reciprocal temperature, the slope of the relationship, considered as an Arrhenius function, indicated an activation energy of ca. 7 kcal mol⁻¹ for the rate-determining step.^{4d} This value may be compared with an estimate (9 kcal mol⁻¹) of the bond dissociation energy of the radical cation obtained from consideration of the thermochemical cycle similar to those shown in Figure 1.^{4c}

The free energy change for the radical cation cleavage (ΔG_C) can be estimated from eq 3 where ΔG_{BDE} represents the bond dissociation free energy of the neutral molecule, ΔG_R is the free energy required for one electron oxidation of the radical fragment, and ΔG_M is the free energy of one electron oxidation of the neutral molecule. The difference in free energy of oxidation ($\Delta G_R - \Delta G_M$) is proportional to the difference in oxidation potential of the radical and the neutral molecule (eq 4). Equation 5 therefore follows.

$$\Delta G_C = \Delta G_{BDE} + \Delta G_R - \Delta G_M \quad (3)$$

$$\Delta G_R - \Delta G_M = F(E_{1/2}^{ox}(R^*) - E_{1/2}^{ox}(R-R)) \quad (4)$$

$$\Delta G_C = \Delta G_{BDE} + F(E_{1/2}^{ox}(R^*) - E_{1/2}^{ox}(R-R)) \quad (5)$$

If, instead of the bond dissociation free energy (ΔG_{BDE}), only the bond dissociation enthalpy (ΔH_{BDE}) is available, eq 5 can be transformed to eq 6. The last term in eq 6 represents the dif-

$$\Delta H_C = \Delta H_{BDE} + F(E_{1/2}^{ox}(R^*) - E_{1/2}^{ox}(R-R)) - T(\Delta S(R-R) - \Delta S(R-R^*)) \quad (6)$$

ference in entropy change for the cleavage of the neutral molecule and the corresponding radical cation. If the reasonable assumption is made that for these large delocalized species solvation of the radical cation is similar to the solvation of the carbocation fragment formed upon cleavage, and if the solvation entropies of the neutral molecule and the radical fragment are also similar

(7) Fluorescence quenching by the electron-transfer process reaches the diffusion-controlled rate when the free energy calculated by eq 1 is <ca. -3 kcal mol⁻¹ (Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259).

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Table IV. Products Formed upon Cleavage of the Radical Cation of Triarylalkanes^a

| triarylalkane | products | rel yield (mol %) | |
|---|--|---|---------|
| 2-methyl-1,1,2-triphenylpropane (14) | diphenylmethane (3) | 50.0 ^b | |
| | cumyl methyl ether (15) | 50.0 ^b | |
| | methyl diphenylmethyl ether (5) | (trace) ^b | |
| | cumene (37) | (trace) ^b | |
| 2-(4-(trifluoromethyl)phenyl)-2-methyl-1,1-diphenylpropane (16) | 4-(trifluoromethyl)cumene (18) | 24.7 | |
| | methyl diphenylmethyl ether (5) | 22.3 | |
| | methyl 4-(trifluoromethyl)cumyl ether (17) | 22.8 | |
| | diphenylmethane (3) | 26.5 | |
| | 2,3-dimethyl-2,3-bis(4-(trifluoromethyl)phenyl)butane (38) | 2.9 | |
| | 1,1,2,2-tetraphenylethane (12) | 0.8 | |
| 1,1,2-triphenylpropane (23) | methyl 1-phenylethyl ether (39) | 42.9 | |
| | diphenylmethane (3) | 42.2 | |
| | ethylbenzene (40) | (trace) | |
| | methyl diphenylmethyl ether (5) | 7.1 | |
| | benzophenone (41) | 0.4 | |
| | benzhydrol (42) | 1.4 | |
| | 2,3-diphenylbutane (meso and racemic) (43) | 0.8 | |
| | 1-(4-cyanophenyl)-1-phenylethane (44) | 3.3 | |
| | 2-(4-cyanophenyl)-2-methyl-1,1-diphenylpropane (24) | 4-cyanocumene (45) | 44.1 |
| | | methyl diphenylmethyl ether (5) | 29.8 |
| | | 4-cyanocumyl methyl ether (46) | 3.8 |
| diphenylmethane (3) | | 22.3 | |
| 2-(4-methoxyphenyl)-2-methyl-1,1-diphenylpropane (25) | diphenylmethane (3) | 50.0 ^b | |
| | 4-methoxycumyl methyl ether (47) | 50.0 ^b | |
| 2-(4-fluorophenyl)-2-methyl-1-(4-methylphenyl)-1-phenylpropane (26) | 4-fluorocumyl methyl ether (48) | 47.2 | |
| | (4-methylphenyl)phenylmethane (32) | 37.8 | |
| | 4-fluorocumene (49) | (trace) | |
| | methyl (4-methylphenyl)phenylmethyl ether (33) | 1.0 | |
| | 2-(4-fluorophenyl)propene (50) | 1.5 | |
| | 2,3-bis(4-fluorophenyl)-2,3-dimethylbutane (51) | 2.3 | |
| | 1,2-bis(4-methylphenyl)-1,2-diphenylethane (52) (meso and racemic) | 2.1 | |
| | 2-(4-cyanophenyl)-2-(4-fluorophenyl)propane (53) | 3.6 | |
| | 4-methylbenzhydrol (55) and 4-methylbenzophenone (54) | 3.7 | |
| | 2-(4-fluorophenyl)-2-propanol (56) | (trace) | |
| | 4-fluorocumyl methyl ether (48) | 47.3 | |
| | 2-(4-fluorophenyl)-2-methyl-1,1-bis(4-methylphenyl)propane (27) | bis(4-methylphenyl)methane (34) | 35.8 |
| | | 4-fluorocumene (49) | (trace) |
| | | methyl bis(4-methylphenyl)methyl ether (35) | 5.1 |
| | | 2-(4-fluorophenyl)propene (50) | 3.1 |
| | | 2,3-bis(4-fluorophenyl)-2,3-dimethylbutane (51) | 1.3 |
| | | 1,1,2,2-tetrakis(4-methylphenyl)ethane (57) | 0.5 |
| 2-(4-cyanophenyl)-2-(4-fluorophenyl)propane (53) | | 3.3 | |
| 4,4'-dimethylbenzhydrol (59) | | 1.8 | |
| 4,4'-dimethylbenzophenone (58) | | 1.5 | |
| 2,2,3-triphenylbutane (28) | | ethylbenzene (40) | (trace) |
| | | methyl 1,1-diphenylethyl ether (36) | 41.7 |
| | 1,1-diphenylethane (60) | 22.6 | |
| | methyl 1-phenylethyl ether (39) | 1.9 | |
| | 2,3-diphenylbutane (meso and racemic) (43) | 12.1 | |
| | 1-(4-cyanophenyl)-1-phenylethane (44) | 11.3 | |
| | 1,1-diphenylethylene (61) | 2.1 | |
| 2-methyl-1-(4-methylphenyl)-1,2-diphenylpropane (29) | cumyl methyl ether (15) | 42.3 | |
| | (4-methylphenyl)phenylmethane (32) | 44.5 | |
| | cumene (37) | (trace) | |
| | methyl (4-methylphenyl)phenylmethyl ether (33) | 1.0 | |
| | 2-phenylpropene (62) | 1.7 | |
| | 2,3-dimethyl-2,3-diphenylbutane (63) | 1.8 | |
| | 1,2-bis(4-methylphenyl)-1,2-diphenylethane (meso and racemic) (52) | 1.6 | |
| | 2-(4-cyanophenyl)-2-phenylpropane (65) | 4.4 | |
| | 4-methylbenzhydrol (55) and 4-methylbenzophenone (54) | 2.7 | |
| 2-methyl-1,1-bis(4-methylphenyl)-2-phenylpropane (30) | cumyl methyl ether (15) | 43.2 | |
| | bis(4-methylphenyl)methane (34) | 38.5 | |
| | cumene (37) | 0.7 | |
| | methyl bis(4-methylphenyl)methyl ether (35) | 6.8 | |
| | 2-phenylpropene (62) | 1.9 | |
| | 2,3-dimethyl-2,3-diphenylbutane (63) | 1.3 | |
| | 1,1,2,2-tetrakis(4-methylphenyl)ethane (57) | 1.4 | |
| | 2-(4-cyanophenyl)-2-phenylpropane (65) | 4.7 | |
| | 4,4'-dimethylbenzhydrol (59) | 0.7 | |
| | 4,4'-dimethylbenzophenone (58) | 0.8 | |
| | 2-phenyl-2-propanol (66) | (trace) | |

Table IV (Continued)

| triarylalkane | products | rel yield (mol %) |
|---|--|-------------------|
| 2-methyl-1,1,2-tris(4-methylphenyl)propane (31) | methyl 4-methylcumyl ether (67) | 44.2 |
| | bis(4-methylphenyl)methane (34) | 38.3 |
| | 4-methylcumene (68) | (trace) |
| | methyl bis(4-methylphenyl)methyl ether (35) | 2.0 |
| | 2-(4-methylphenyl)propene (69) | 4.0 |
| | 2,3-dimethyl-2,3-bis(4-methylphenyl)butane (70) | 4.4 |
| | 1,1,2,2-tetrakis(4-methylphenyl)ethane (57) | 0.7 |
| | 2-(4-cyanophenyl)-2-(4-methylphenyl)propane (71) | 3.7 |
| | 4,4'-dimethylbenzhydrol (59) | 1.1 |
| | 4,4'-dimethylbenzophenone (58) | 1.6 |

^aSolutions of the triarylalkane (0.10 M) and 1,4-dicyanobenzene (2) (0.02 M) in acetonitrile-methanol (3:1) were irradiated at 80 °C. ^bReference 4d.

to each other (or are relatively small compared to the entropies of the charged species), this entropy term will be small, and the enthalpy for the bond cleavage in step 4 can then be estimated from eq 7. When $\Delta S(R-R) \approx \Delta S(R-R^+)$

$$\Delta H_C = \Delta H_{BDE} + F(E_{1/2}^{ox}(R^*) - E_{1/2}^{ox}(R-R)) \quad (7)$$

The thermochemical cycle represented by eq 7 is shown pictorially in Figure 1.

Relating the calculated bond dissociation enthalpy to the rate of cleavage of the radical cation requires the further assumption that there is no additional activation energy for this process. That is, that there is no activation energy for the reverse reaction of the radical fragment with the carbocation. While this may be true for reaction in the gas phase, in solution there may be some activation energy associated with solvent reorganization, particularly in polar solvent.¹⁰ Nevertheless, we can show that this thermochemical cycle may be used, as the first approximation, to predict reactivity.^{4,11}

Thus, the estimated bond dissociation enthalpy (ΔH_C) for cleavage of the radical cation of 2-methyl-1,1,2-triphenylpropane (14) is only 5 kcal mol⁻¹ (Figure 1a)—cleavage occurs upon irradiation at 10 °C. For 1,1,2-triphenylpropane (23), $\Delta H_C = 13$ kcal mol⁻¹, and cleavage is relatively inefficient at 10 °C and more efficient at 80 °C. The radical cation of 1,1,2-triphenylethane (13), estimated $\Delta H_C = 17$ kcal mol⁻¹, does not cleave even when the irradiation is carried out at 80 °C. The temperature dependence of the efficiency of the cleavage of 19 and 21 is clear from the data in Tables I and II. The thermochemical cycles for these molecules are similar to that for 1,1,2,2-tetraphenylethane (12).^{4c,12}

There is now enough evidence to firmly establish the upper threshold of ΔH_C above which radical cation cleavage will be inefficient, relative to back electron transfer, when the irradiation is carried out under these standard conditions. If ΔH_C , estimated by eq 7, is >15 kcal mol⁻¹ radical cation cleavage by this method will be inefficient.

Factors in addition to ΔH_C can influence the rate of cleavage of radical cations. In rigid molecules, where the singly occupied molecular orbital (SOMO) and the α -carbon-carbon bond are unable to adopt a periplanar orientation, cleavage of the radical cation is inhibited.^{4b} The arylalkanes shown in Chart I are free to rotate around the α -carbon-carbon bond. The required con-

formation is favorable. There are also other reactions of the radical cation that can compete with carbon-carbon bond cleavage. For example, if the proton bound to the α -carbon (benzylic) is acidic, deprotonation may compete favorably with α -carbon-carbon bond cleavage.¹³ Deprotonation is favored in basic media and is insignificant in the cases studied here.

What Factors Determine Which Fragment Will Ultimately Be Incorporated into the Hydrocarbon and Which Will Be Incorporated into the Ether? With unsymmetric radical cations the cleavage process (step 4) may occur in both directions giving alternative pairs of carbocations and radicals. Previous results have led to the conclusion that the carbocation product is preferentially derived from the radical fragment that has the lower oxidation potential. Not enough data were available at the time to firmly establish the quantitative relationship between the difference in the oxidation potential of the two possible fragments and the product ratio.^{4c,d} Two mechanisms have been considered: (step 4a in Scheme II) the product ratio may be determined by the relative rates of the two possible cleavage pathways or by rapid equilibration of the carbocations and radicals within the geminate radical ion pair, or, (step 4b in Scheme II) equilibrium may be established upon reencounter of the freely solvated radicals and carbocations. The results reported here indicate clearly that the product ratio is established within the geminate radical ion pair (step 4a in Scheme II).

The ratio (r_i) of the intermediate radicals and carbocations determined during the radical cation cleavage process, or attained upon equilibration within the geminate radical ion pair (these two processes are indistinguishable, step 4a in Scheme II), can be represented by eq 8, where ΔG_1 and ΔG_2 are the free energy differences for the two alternative modes of fragmentation (step 4a in Scheme II). If both sets of radicals and carbocations are similar in extent of delocalization and solvent affinity, such that the solvent reorganization free energies at the transition states are of the same magnitude, then the differences in free energy can be expressed by eq 9. Finally, in the case of "ideal" behavior, when the radicals and carbocations are rapidly and quantitatively scavenged by subsequent reactions (steps 5, 6, and 7 in Scheme II) so that the product ratio (r_p) obtained from either the hydrocarbons or the ethers is equal to the initial ratio of the intermediates within the geminate radical ion pair (r_i), eq 11 follows.

$$r_i = \frac{[R^*]}{[R^+]} = \frac{[R^+]}{[R^*]} = e^{-(\Delta G_1 - \Delta G_2)/RT} \quad (8)$$

$$\Delta G_1 - \Delta G_2 = F(E_{1/2}^{ox}(R^*) - E_{1/2}^{ox}(R^+)) \quad (9)$$

$$r_p = \frac{[R^*H]}{[RH]} = \frac{[RNu]}{[R^+Nu]} \quad (10)$$

When $r_p = r_i$

$$\ln r_p = \frac{F}{RT} (E_{1/2}^{ox}(R^*) - E_{1/2}^{ox}(R^+)) \quad (11)$$

(9) The bond dissociation energy of 1,1,2-triphenylpropane (13) was obtained by subtracting the heat of formation of 13 (53.08 kcal mol⁻¹) from the heats of formation of the diphenylmethyl radical (68.11 kcal mol⁻¹) and the 1-phenylethyl radical (40.47 kcal mol⁻¹). The heats of formation were obtained by using the modified MM2 program. (a) Ruchardt, C.; Beckhaus, H.-D. *Top. Curr. Chem. Org. Chem.* **1986**, *130*, 1. (b) Iman, M. R.; Allinger, N. L. *J. Mol. Struct.* **1985**, *126*, 345.

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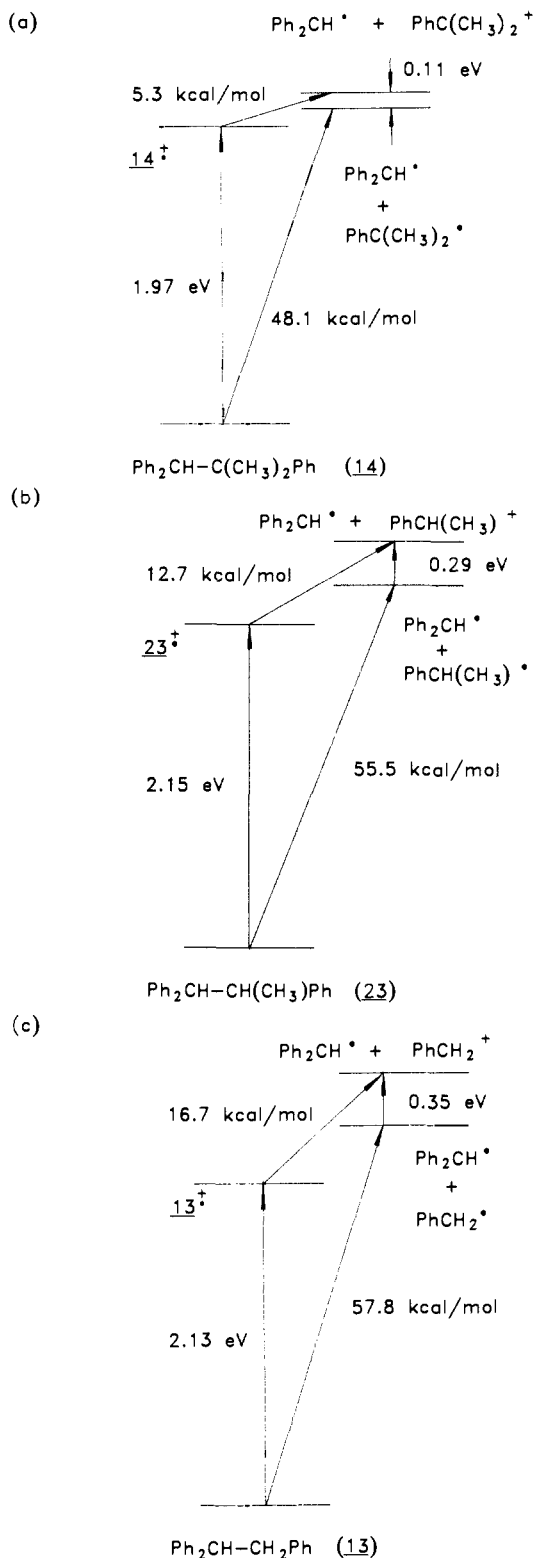


Figure 1. Thermochemical cycles useful for estimating the bond dissociation energy of the radical cations of (a) 2-methyl-1,1,2-triphenylpropane (14), (b) 1,1,2-triphenylpropane (23), and (c) 1,1,2-triphenylethane (13). Data taken from ref 3, 4, and 9.

where F = Faraday constant, R = gas constant, and T is absolute temperature.

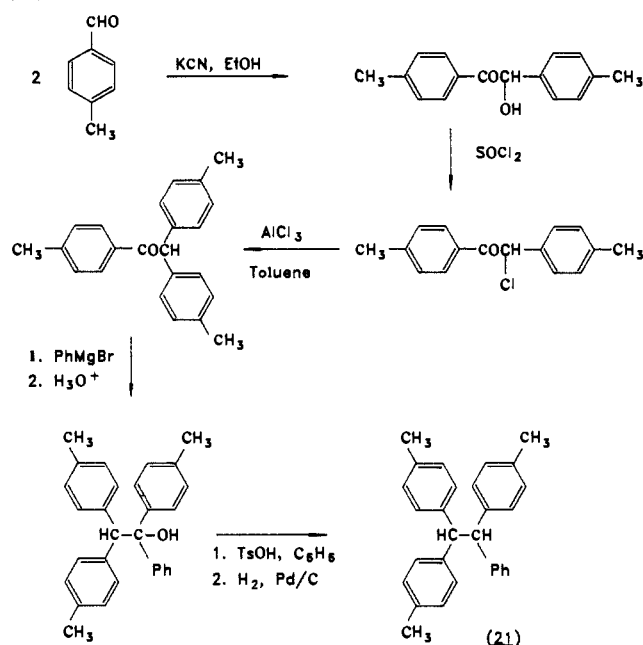
The reactivity of the radical cations of the methyl-substituted tetraphenylethanes **19**, **20**, and **21** exemplify this "ideal" behavior. The data in Tables I and II illustrate that the product ratios based upon the hydrocarbon and upon the ether products are in good agreement. The differences in oxidation potential between the diphenylmethyl radical and the (4-methylphenyl)phenylmethyl radical and between the (4-methylphenyl)phenylmethyl radical

Table V. Oxidation Potential Differences between the Fragment Radicals Obtained upon Cleavage of the Radical Cations of 1-(4-Methylphenyl)-1,2,2-triphenylethane (**19**) and 1,1,2-Tris(4-methylphenyl)-2-phenylethane (**21**) Determined from the Product Ratios

| Temp (°C) | 19 ^{•+} ($E_{1/2}^{ox}(R^•) - E_{1/2}^{ox}(R'^•)$) ^a (V) | 21 ^{•+} ($E_{1/2}^{ox}(R^•) - E_{1/2}^{ox}(R''^•)$) ^b (V) |
|-----------|---|--|
| 80 | 0.075 | 0.079 ± 0.001 |
| 75 | 0.073 | |
| 70 | 0.083 | |
| 65 | 0.088 | 0.079 ± 0.002 |
| 60 | 0.083 | |
| 55 | 0.083 | |
| 50 | 0.088 | 0.078 ± 0.0008 |
| 40 | 0.086 | |
| 35 | | 0.078 ± 0.0005 |
| 20 | | 0.076 ± 0.001 |

^a $R^•$ = diphenylmethyl radical; $R'^•$ = (4-methylphenyl)phenylmethyl radical. ^b $R^•$ = (4-methylphenyl)phenylmethyl radical; $R''^•$ = bis(4-methylphenyl)methyl radical.

Scheme III. Synthesis of 1,1,2-Tris(4-methylphenyl)-2-phenylethane (**21**)



and the bis(4-methylphenyl)methyl radical calculated (eq 11) from the product ratios are listed in Table V.

While the product ratios depend upon temperature (Tables I, II, and III), the differences in oxidation potential of the pairs of radicals are relatively constant over the temperature range studied. The difference in the oxidation potential of the (4-methylphenyl)phenylmethyl radical and the bis(4-methylphenyl)methyl radical, for example, varies by only 3 mV (ca. 4%) over a 60 K temperature range, while the product ratios vary by almost a factor of 2. (The effect of temperature on the product ratio will be discussed in greater detail below.) This is good evidence that the product ratios reflect differences in the oxidation potentials of the fragment radicals.

If the difference in oxidation potential of the two radical fragments is known, the product ratio from the cleavage of the radical cation can be predicted from eq 11. The corollary follows; if the product ratio from the cleavage of a radical cation can be measured, the relative oxidation potentials of the two radical fragments can be determined.

The product ratio expected from the cleavage of the radical cation of 1,1-bis(4-methylphenyl)-2,2-diphenylethane (**20**) can be calculated from the difference in oxidation potential between the diphenylmethyl and the bis(4-methylphenyl)methyl radicals (0.16 V, Table VI) by using eq 11. The calculated ratio (ca. 500 at 25 °C) is consistent with the experimental observation; only

Table VI. Oxidation Potentials of Some Diarylmethyl Radicals

| radical | $E_{1/2}^{\text{ox}}(\text{R}^{\bullet})^a$ | $\frac{E_{1/2}^{\text{ox}}(\text{R}^{\bullet}) - E_{1/2}^{\text{ox}}(\text{R}'^{\bullet})}{E_{1/2}^{\text{ox}}(\text{R}'^{\bullet})}$ | $E_{1/2}^{\text{ox}}(\text{R}^{\bullet})^b$ |
|------------------------------|---|---|---|
| diphenylmethyl | 0.35 | 0.07 ^c 0.085 ^d | 0.350 |
| (4-methylphenyl)phenylmethyl | 0.28 | | 0.265 ± 0.002 |
| bis(4-methylphenyl)methyl | 0.23 | 0.05 ^c 0.077 ^d | 0.188 ± 0.003 |

^a determined by the modulated photolysis/phase sensitive voltammetry method in acetonitrile (V vs SCE). Estimated error ±0.01 V. Reference 3d. ^b Determined from the ratio of products obtained upon cleavage of the radical cations of 1-(4-methylphenyl)-1,2,2-triphenylethane (**19**) and 1,1,2-tris(4-methylphenyl)-2-phenylethane (**21**) at 25 °C (Table V) by using eq 11. ^c Calculated from the oxidation potentials listed in the column to the left. ^d Calculated from the differences in oxidation potential determined from the product ratio shown in the column to the right and using the value for diphenylmethyl (0.350 V) as the primary standard.

diphenylmethane (**3**) and methyl bis(4-methylphenyl)methyl ether (**35**) were detected. This result illustrates one of the limitations of this method for the determination of differences in oxidation potential of radicals. The product ratio is so dependent upon the difference in the oxidation potentials of the two fragment radicals that the ratio cannot be determined accurately if the difference is greater than ca. 0.1 V. This is also the case with the cleavage of 1,1,2,2-tetraphenylpropane (**22**). The ratio of methyl 1,1-diphenylethyl ether (**36**) to methyl diphenylmethyl ether (**5**) is too large to measure accurately. The oxidation potential of the 1,1-diphenylethyl radical must be at least 0.1 V less than that of the diphenylmethyl radical. Conversely, the method allows the precise determination of differences in oxidation potentials of two radicals when these differences are small. A product ratio of 1.2 (or 0.8) is easily measured and would indicate that the oxidation potentials differ by only 5 mV.

Only relative oxidation potentials can be determined by this method; to obtain absolute values requires reference to standard potentials determined by some other method. The electrochemical measurement of radical oxidation potentials is not a simple experiment. The potentials generally cannot be determined directly because of the reactivity of both the radicals and the carbocations in solution. Wayner and Griller have recently developed a new approach for measuring the oxidation potentials of radicals, modulated photolysis/phase sensitive voltammetry, that offers many advantages over earlier methods.³ The oxidation potentials of the diphenylmethyl, the (4-methylphenyl)phenylmethyl, and the bis(4-methylphenyl)methyl radicals, determined by this method, are shown in Table VI. The difference in oxidation potential between these radicals, determined by the electrochemical method and the difference calculated from the product ratios at 25 °C, using eq 11, is in good agreement (±30 mV, more accurate than the experimental error in the electrochemical method justifies). The oxidation potential of the diphenylmethyl radical, 0.350 V vs SCE, has been chosen as the primary standard for this photochemical method, against which the oxidation potentials of the other radicals will be measured. The (4-methylphenyl)phenylmethyl radical and the bis(4-methylphenyl)methyl radical then become secondary standards for this method.

The alternative possibility, that the product ratio is determined by reencounter equilibration of radicals and carbocations (step 4b in Scheme II), can be dismissed. Equation 12 (the Nernst equation) would indicate the position of this equilibrium. Again, assuming the product ratio reflects the ratio of intermediates and in the event (unlikely) that the intermediates subsequently react at essentially the same rate, the product ratio would be represented by eq 13 which differs from eq 11 by a factor of two (in the denominator of eq 13). The calculated differences in oxidation potential between the diphenylmethyl radical relative to the (4-methylphenyl)phenylmethyl radical and between the (4-methylphenyl)phenylmethyl radical and the bis(4-methylphenyl)methyl radical, obtained by substituting the product ratios in eq 13, do not agree with the differences determined by the

electrochemical method. Equation 13 overestimates these differences by more than 100 mV. If the rates of subsequent reactions of the intermediates were not identical, the equilibrium would be driven toward the more reactive intermediate, and the product ratio would then be a complicated function, not directly related to the difference in oxidation potential of the two radicals. It also seems unlikely, in view of the very low concentration of the intermediates and the relatively rapid rate of the subsequent reactions, that equilibrium by step 4b (in Scheme II) could be established.

$$\ln K_i = \frac{F}{RT} (E_{1/2}^{\text{ox}}(\text{R}'^{\bullet}) - E_{1/2}^{\text{ox}}(\text{R}^{\bullet})) \quad (12)$$

Since $r_i = K_i^{1/2}$, and, when $r_i = r_p$

$$\ln r_p = \frac{F}{2RT} (E_{1/2}^{\text{ox}}(\text{R}'^{\bullet}) - E_{1/2}^{\text{ox}}(\text{R}^{\bullet})) \quad (13)$$

Step 5, reaction of the carbocation with a nucleophile, has received considerable attention recently.¹⁴ The more stable, more delocalized, carbocation reacts slower. While the rate constant for reaction of the 1-phenylethyl cation with water in acetonitrile is essentially diffusion-controlled, the rate of reaction of the more delocalized diphenylmethyl cation ($1.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) is significantly less than diffusion-controlled, and the bis(4-methylphenyl)methyl cation reacts even slower ($4.3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$).¹⁴ If equilibration of the alternative pairs of radicals and carbocations were occurring (step 4b), the ether derived from the less stable, more reactive carbocation would dominate. In the solvent mixture used here (acetonitrile-methanol, 3:1; ca. 6 M methanol) reaction of the carbocation with methanol must be rapid enough to prevent reencounter of the cations and radicals. The reaction of these carbocations with acetonitrile, to give products ultimately resulting from the nitrilium ion, is considerably slower (10^4 – $10^5 \text{ M}^{-1} \text{ s}^{-1}$) than reaction with methanol.^{14a} Equating the ratio of ethers (r_p) to the ratio of intermediates (r_i) requires that with those carbocations that have a β -hydrogen, loss of a proton is slow relative to reaction with methanol. This is a valid assumption for reaction in this nonbasic nucleophilic solvent mixture.¹⁵

Step 6 of the reaction scheme represents the reduction of the radical by the radical anion of the sensitizer. Even when this process is thermodynamically favorable and occurs at the diffusion-controlled rate, the low probability of an encounter involving these two reactive species, both present initially in low concentration, may allow other reactions to compete. Variable amounts of products expected from the radical, such as coupling and disproportionation products, are in fact detected. When the radical is consumed in this way the concentration of the more persistent radical anion will increase, and the rate of step 6 will increase proportionately. This is then an example of a reaction controlled by "internal suppression of fast modes".^{16a}

In the ideal cases discussed so far, the reduction potential of the diarylmethyl radical has been significantly less than that of the sensitizer; the reduction potential of the diphenylmethyl radical is -1.14 V ,^{3b,17} while the reduction potential of **2** is -1.66 V .² In these cases, products resulting from reactions of the radicals other than reduction (step 6 in Scheme II) are minor, and the ratio of products (r_p) from the carbocations equals the ratio of products derived from the radicals. When cleavage of the radical cation of the triarylalkanes occurs in the direction to give the arylalkyl radical, this condition is not met and the increased complexity of the reaction mixtures reflects this difference. The reduction

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(15) (a) Richard, J. P.; Jencks, W. P. *J. Am. Chem. Soc.* **1984**, *106*, 1373. (b) Schubert, W. H.; Keeffe, J. R. *J. Am. Chem. Soc.* **1972**, *94*, 559. (c) Schubert, W. M.; Lamm, B. *J. Am. Chem. Soc.* **1966**, *88*, 120.

(16) (a) Fischer, H. *J. Am. Chem. Soc.* **1986**, *108*, 3925. (b) Lan, J. Y.; Schuster, G. B. *Tetrahedron Lett.* **1986**, *27*, 911.

(17) (a) Breslow, R.; Grani, J. L. *J. Am. Chem. Soc.* **1977**, *99*, 7745. (b) Bank, S.; Schepartz, A.; Giannateo, P.; Zubieta, J. A. *J. Org. Chem.* **1983**, *48*, 3458.

potential of the 1-phenylethyl radical (−1.60 V) is almost the same as that of **2**, and the reduction potential of the cumyl radical (−1.73 V) is somewhat greater.^{3b} Even when an unfavorable equilibrium is established at step 6 (in Scheme II), reaction can be driven toward the hydrocarbon by rapid protonation of the anion (step 7 in Scheme II); but, other reactions of the radical may be able to compete.

The side products listed in Table IV can be accounted for by other reactions of the radical occurring in competition with reduction (step 6 in Scheme II). These include the radical coupling and disproportionation products, products resulting from the radical reacting with adventitious oxygen, and products resulting from addition of the radical to the 1,4-dicyanobenzene radical anion at the ipso position followed by loss of cyanide anion. When these side products constitute a significant percentage of the reaction mixture, the ratios of the products (r_p) arising from the carbocations and from the radicals do not agree, and then the ratio of ethers provides the better indication of the initial ratio of intermediates (r_i).

The Effect of Temperature on the Product Ratio. As we have seen, both the efficiency of the cleavage of radical cations and the ratio of products (r_p) are temperature dependent. If cleavage of a radical cation is too inefficient at room temperature, the determination of r_p can be carried out at higher temperatures; however, the product ratio must then be extrapolated to the 25 °C value because, by convention, standard oxidation potentials refer to this temperature. How large is the effect of temperature on the relative oxidation potentials of radicals, and what factors influence the magnitude of this effect?

Temperature enters into eq 11 at two places: the logarithm of the product ratio is inversely proportional to the temperature, and the difference between the oxidation potentials of the radical fragments can (and generally does) depend upon the temperature. The negative of the first derivative of the free energy versus temperature is equal to entropy (eq 14). The first derivative of eq 9 versus temperature will be proportional to the entropy change (eq 15).

$$\frac{d(\Delta G)}{dT} = -\Delta S \quad (14)$$

$$\frac{d(\Delta E^{\text{ox}})}{dT} = \frac{1}{F} \Delta S \quad (15)$$

where

$$\Delta E^{\text{ox}} = E_{1/2}^{\text{ox}}(\text{R}^+) - E_{1/2}^{\text{ox}}(\text{R}^{\bullet})$$

It is hard to predict whether the entropy change for the electron exchange process between the radical and the carbocation is constant, or whether it also depends upon the temperature; however, when the dependence of the change in oxidation potential on the temperature is approximately linear, the slope of the relationship will be proportional to the average entropy change within the temperature range studied (eq 16). Similarly, the logarithm of the product ratio (r_p) can be expressed as a function of temperature, in terms of the average entropy change, by eq 17.

$$\Delta E^{\text{ox}} = \Delta E_0^{\text{ox}} + \frac{\Delta S}{F}(T - T_0) \quad (16)$$

$$\ln(r_p) = \ln(r_p)_0 + \frac{\Delta S}{RT}(T - T_0) \quad (17)$$

where ΔE^{ox} and ΔE_0^{ox} are the oxidation potential differences at the temperatures T and T_0 , and (r_p) and $(r_p)_0$ are the product ratios at T and T_0 , respectively.

The average entropy change for the electron exchange process between the fragment radical and carbocation, within the radical-carbocation pair, estimated from the slope of the linear correlation of the oxidation potential differences with temperature, are summarized in Table VII.

Some factors which affect the magnitude of the entropy change are evident, even from this limited amount of data. The entropy change for the electron exchange process involving a tertiary cumyl radical and a secondary diphenylmethyl carbocation is significantly

Table VII. Entropy Changes for the Electron Exchange between Radicals and Cations in Acetonitrile–Methanol (3:1) Solution and Their Effect on the Radical Oxidation Potential Difference

| $\text{R}^{\bullet} + \text{R}^+ \rightarrow \text{R}^+ + \text{R}^{\bullet}$ | | ΔS (cal mol ^{−1} K ^{−1}) | $E_{333\text{K}}^{\text{ox}} - \Delta E_{293\text{K}}^{\text{ox}}$ (mV) |
|---|---|---|---|
| 4-CH ₃ (C ₆ H ₄)C•(C ₆ H ₅)H | (4-CH ₃ (C ₆ H ₄) ₂ C•H | 1.1 ± 0.3 | 2.8 |
| (C ₆ H ₅) ₂ C•H | (C ₆ H ₅)C•(CH ₃)H | −3.6 ± 1.4 | −9.4 |
| (C ₆ H ₅) ₂ C•H | 4-NC(C ₆ H ₄)C•(CH ₃) ₂ | −6.9 ± 0.4 | −18 |
| (C ₆ H ₅) ₂ C•H | 4-F ₃ C(C ₆ H ₄)C•(CH ₃) ₂ | −5.0 ± 1.4 | −13 |
| (4-CH ₃ (C ₆ H ₄) ₂ C•H | 4-F(C ₆ H ₄)C•(CH ₃) ₂ | −6.8 ± 0.3 | −18 |
| (4-CH ₃ (C ₆ H ₄) ₂ C•H | (C ₆ H ₅)C•(CH ₃) ₂ | −7.5 ± 1.5 | −19 |
| 4-CH ₃ (C ₆ H ₄)C•(C ₆ H ₅)H | 4-F(C ₆ H ₄)C•(CH ₃) ₂ | (−7.9) ^a | −20 |
| 4-CH ₃ (C ₆ H ₄)C•(C ₆ H ₅)H | (C ₆ H ₅)C•(CH ₃) ₂ | (−6.1) ^a | −16 |
| (C ₆ H ₅)C•(CH ₃)H | (C ₆ H ₅) ₂ C•(CH ₃) | −0.6 ± 0.3 | −1.5 |

^aThese values are based upon relatively high product ratios.

negative and of the same order of magnitude (−5 and −8 cal mol^{−1} K^{−1}). This may indicate that solvent orientation is similar around carbocations of similar size or extent of charge delocalization. When the radicals and carbocations are of the same order (e.g., (4-methylphenyl)phenylmethyl and 1-phenylethyl, both secondary), the magnitude of the entropy change for the electron exchange process decreases. When the extent of solvation and charge delocalization in both carbocations and radicals are similar (e.g., (4-methylphenyl)phenylmethyl and bis(4-methylphenyl)methyl), the relative oxidation potential differences become almost independent of temperature.

In general, the effect of temperature on the relative oxidation potentials of radicals is small (≤20 mV for a temperature change of 60 K). Nevertheless, when small differences in oxidation potentials are involved, as in the case of 2-(4-(trifluoromethyl)phenyl)-2-methyl-1,1-diphenylpropane (**16**), a 20-mV difference in oxidation potential is significant. If the radical cation cleavage is to be applied for the determination of the standard oxidation potential of a radical, and if the cleavage cannot be carried out at 25 °C, the radical cation chosen as a precursor should cleave to give fragments of the same order (i.e., both primary, secondary, or tertiary) and of similar size in order to minimize the influence of temperature on the relative oxidation potential differences. Otherwise, the cleavage should be carried out over a temperature range and the product ratio extrapolated to the standard temperature.

Correlation of the Oxidation Potentials of Radicals Determined from the Product Ratios Obtained upon Cleavage of the Radical Cation with Those Determined by the Electrochemical Method. Results from the cleavage of the radical cations exemplified in Table IV allow the determination of the oxidation potentials of three additional arylmethyl radicals—the 1,1-diphenylethyl, the 1-phenylethyl, and the cumyl radicals—for which electrochemical oxidation potentials are available.

Only an upper limit for the oxidation potential of the 1,1-diphenylethyl radical of <0.25 V (vs SCE) could be determined from the product ratio obtained upon cleavage of 1,1,2,2-tetra-phenylpropane (**22**). The radical cation of 1,1-bis(4-methylphenyl)-2,2-diphenylpropane should give the measurable ratio of products required for a more exact determination. However, because of the anticipated thermal instability of this 1,1,2,2-tetraarylpropane, cleavage of the radical cation of 2,2,3-triphenylbutane (**28**) was studied instead. Substituting the ratio (r_p) of methyl 1,1-diphenylethyl ether (**36**) to methyl 1-phenylethyl ether (**39**) obtained upon cleavage of the radical cation of **28** in eq 11 gives a difference in the oxidation potentials of the 1-phenylethyl radical and the 1,1-diphenylethyl radical of 0.095 V (the latter radical having the lower oxidation potential). In like manner, from the product ratio obtained upon cleavage of 1,1,2-triphenylpropane (**23**) the difference in oxidation potentials of the diphenylmethyl radical and the 1-phenylethyl radical was determined, 0.063 V (the latter radical having the lower oxidation potential). Accepting the oxidation potential of diphenylmethyl radical (0.350 V) as the primary standard establishes the oxidation potentials of the 1-phenylethyl radical (0.287 V) and of the

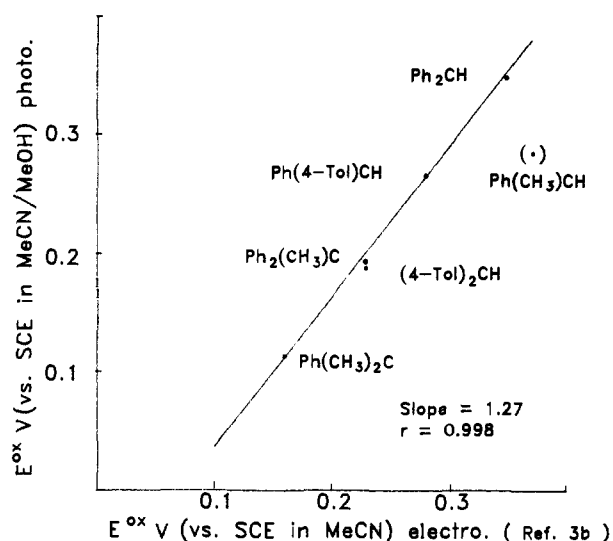


Figure 2. A comparison of the oxidation potentials determined by the electrochemical method and by the photochemical method.

1,1-diphenylethyl radical (0.192 V). The value determined for the oxidation potential of the 1,1-diphenylethyl radical is consistent with the upper limit established from the product ratio obtained upon cleavage of **22**.

Cleavage of the radical cation of 2-methyl-1,1,2-triphenylpropane (**14**) gives a good yield of diphenylmethane (**3**) and cumyl methyl ether (**15**).^{4d} The difference in the oxidation potentials of the two possible radical fragments must be too large to afford a measurable ratio of all four of the cleavage products, and when the difference (0.19 V) in the electrochemically determined oxidation potentials of the cumyl and diphenylmethyl radicals is substituted in eq 11, the calculated ratio of cumyl methyl ether to methyl diphenylmethyl ether is $>10^3$. The oxidation potential of the diphenylmethyl radical is lowered by substitution with a 4-methyl substituent. Cleavage of the radical cation of 2-methyl-1-(4-methylphenyl)-1,2-diphenylpropane (**29**) does give some methyl (4-methylphenyl)phenylmethyl ether (**33**), but the ratio is still too large for an accurate measurement. The oxidation potential of the cumyl radical can be determined accurately from the product ratio obtained upon cleavage of the radical cation of 2-methyl-1,1-bis(4-methylphenyl)-2-phenylpropane (**30**). The ratio of cumyl methyl ether (**15**) to methyl bis(4-methylphenyl)methyl ether (**35**) indicates a difference in oxidation potential of the bis(4-methylphenyl)methyl radical and the cumyl radical of 0.074 V (the latter radical having the lower oxidation potential). Accepting the oxidation potential of bis(4-methylphenyl)methyl radical as a secondary standard (0.188 V) establishes the oxidation potential of the cumyl radical (0.114 V).

Values for the oxidation potential of the 1,1-diphenylethyl radical (0.23 V) and the cumyl radical (0.16 V), determined by the electrochemical method, agree well with these results, but the value reported for the 1-phenylethyl radical (0.37 V) is significantly different (this point has been excluded from the analysis that follows).^{3b} Figure 2 is an illustration of the relationship between the oxidation potentials determined from the product ratios, using eq 11, and by the electrochemical method. The linear correlation (eq 18) of the oxidation potentials, determined by both methods, is excellent ($r = 0.998$). The slope is close to unity. The deviation from unit slope can be accounted for by the variation in experimental conditions (different solvent systems, effects due to the electrode, electrolyte, etc.). The intercept (-0.095) indicates the potential of a hypothetical saturated calomel electrode in acetonitrile-methanol (3:1) solution. The oxidation potentials determined by this method are relative to the electrochemically determined oxidation potential of the diphenylmethyl radical (0.350 V vs SCE).

$$E_{1/2}^{\text{ox}}(R^{\cdot}, \text{V vs SCE})_{\text{photo}} = 1.27E_{1/2}^{\text{ox}}(R^{\cdot}, \text{V vs SCE})_{\text{electro}} - 0.095 \quad (18)$$

Table VIII. Oxidation Potentials of Some Substituted Cumyl Radicals Determined by the Photochemical Method in Acetonitrile-Methanol Solution

| substituent | reference radical | $E_{1/2}^{\text{ox}}(R^{\cdot} \text{ vs SCE})$ | σ^+ ^a |
|-------------------|-------------------|---|-------------------------|
| 4-CN | b | 0.396 ± 0.001 | 0.67 |
| 4-CF ₃ | b | 0.339 ± 0.003 | 0.58 |
| H | d | 0.114 ± 0.004 | 0 |
| H | c | $(0.135 \pm 0.002)^e$ | 0 |
| 4-F | d | 0.108 ± 0.006 | -0.07 |
| 4-F | c | $(0.129 \pm 0.004)^e$ | -0.07 |
| 4-Me | d | 0.081 | -0.26 |

^a Reference 19. ^b Diphenylmethyl. ^c (4-Methylphenyl)phenylmethyl. ^d Bis(4-methylphenyl)methyl. ^e Values determined from high product ratios ($r_p > 100$).

There is a discrepancy in the oxidation potential of the 1-phenylethyl radical determined by the photochemical method (0.287 V) and by the electrochemical method (0.37 V).^{3b} While there is no sound basis for favoring one value over the other, the lower value reported here is internally consistent. The relative effect of an adjacent phenyl and methyl group on the oxidation potential of the benzyl and the 1-phenylethyl radical can be compared. By using the oxidation potentials obtained from the electrochemical method, in the benzyl radical series the oxidation potential of the benzyl radical (0.73 V) is lowered by an adjacent phenyl group in the diphenylmethyl radical (0.35 V) by more than an adjacent methyl group in the 1-phenylethyl radical (0.37 V). In the 1-phenylethyl radical series the order is reversed; the cumyl radical has a lower oxidation potential (0.16 V) than the 1,1-diphenylethyl radical (0.23 V). The relative effects of phenyl versus methyl are consistent when the photochemically derived oxidation potentials are used; the methyl group lowers the oxidation potential by more than the phenyl group, in both series. The gas-phase ionization potential of the 1-phenylethyl radical (6.9 V) is also lower than that of the diphenylmethyl radical (7.56 and 7.32 V).¹⁸

The Effect of Substituents on the Oxidation Potential of Cumyl Radicals. By taking advantage of the variation in oxidation potentials of the standard radicals (diphenylmethyl, (4-methylphenyl)phenylmethyl, and bis(4-methylphenyl)methyl), it is possible to choose a radical cation that will cleave to give a measurable ratio of products (r_p), and thus determine the oxidation potential of other radicals. For example, while 2-methyl-1,1,2-triphenylpropane (**14**) cleaves to give only cumyl methyl ether (**15**) and diphenylmethane (**3**), substitution of an electron-withdrawing group on the cumyl moiety increases the oxidation potential of that fragment to the point where all four products are formed and the product ratio (r_p) can be accurately measured. Cleavage of the radical cation of 2-(4-(trifluoromethyl)phenyl)-2-methyl-1,1-diphenylpropane (**16**) gives all four products (**3**, **5**, **17** and **18**) in almost equal amounts. Cleavage of 2-(4-cyanophenyl)-2-methyl-1,1-diphenylpropane (**24**) gives all four products, but in this case the ratio of methyl diphenylmethyl ether (**5**) to 4-cyanocumyl methyl ether (**46**) is greater than one. The distribution of products formed upon cleavage of the radical cations of the 2-(4-fluorophenyl) derivatives **26** and **27** follows the same pattern as that observed with the mono- and dimethyl derivatives of the unsubstituted cumyl system **29** and **30**. The oxidation potentials of the substituted cumyl radicals listed in Table VIII were determined from the ratio of products obtained upon cleavage of the corresponding precursor radical cations (Table IV) (determined over the temperature range 20–80 °C and interpolated to 25 °C).

A good linear correlation is obtained when the oxidation potentials of these cumyl radicals is plotted against Brown's σ^+

(18) The gas-phase ionization potentials of the 1-phenylethyl and diphenylmethyl radicals are indirectly available from the appearance potentials of the carbocations and the corresponding bond dissociation energies of the hydrocarbons. (a) McLoughlin, R. G.; Morrison, J. D.; Traeger, J. C. *Org. Mass. Spec.* **1979**, *14*, 104. (b) McMillen, D. F.; Golden, D. M. *Ann. Rev. Phys. Chem.* **1982**, *33*, 493. (c) Harrison, A. G.; Lossing, F. P. *J. Am. Chem. Soc.* **1960**, *82*, 1052.

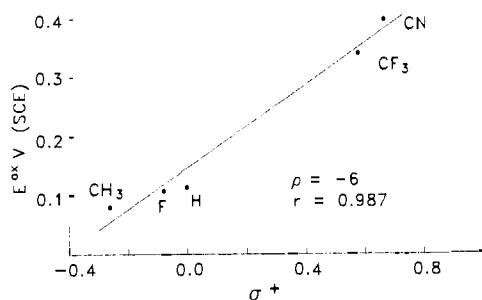


Figure 3. The oxidation potentials of some 4-substituted cumyl radicals versus σ^+ .

substituent constants (Figure 3).^{19b,c} The slope of this line, expressed as a ρ value (eq 19, $\rho = -6$), is large and negative which is appropriate for the development of a carbocation from a neutral radical in solution where interaction with the solvent stabilizes the charge. Compare, for example, the ionization potentials of substituted benzyl radicals which correlate with σ^+ giving a ρ value of -20 .²⁰ In the gas-phase ionization process the positive charge is fully developed on the carbocation, and no solvent stabilization is possible; therefore, this larger reaction constant is expected. The ρ value for the S_N1 solvolysis of substituted cumyl chlorides in 95% aqueous acetone is -4.5 .^{19b,c} A smaller ρ value is expected in this case, consistent with some stabilization of the carbocation as part of the ion pair.

$$E_{1/2}^{\text{ox}}(\text{R}_\text{H}^{\bullet}) - E_{1/2}^{\text{ox}}(\text{R}_\text{X}^{\bullet}) = \frac{2.303RT\rho}{F} \sigma^+ \quad (19)$$

The observed substituent effect on the oxidation potential of a radical represents the combined effect of the substituent on the stability of the radical and on the carbocation. Therefore, a two-parameter correlation involving both σ^+ and σ^* might be expected to give a better fit with the data. In fact, this two parameter correlation is no better than the correlation with σ^+ alone. This is perhaps not surprising, the effect of a substituent on the stability of a radical is insignificant in comparison to the effect on a carbocation.¹²

The Scope and Limitations of the Photosensitized (Electron Transfer) Radical Cation Cleavage Process. This is obviously a complex multistep process. Nevertheless, each step of the mechanism has been analyzed, and the criteria required in order to predict reactivity, under the standard reaction conditions used here, have been identified.

(1) Normally the absorption spectrum of the electron-accepting photosensitizer extends beyond that of the donor in order to allow selective excitation of the acceptor. There is, however, no reason (a priori) why the donor cannot be initially excited instead of the acceptor. One of the necessary attributes of the photosensitizer is a lack of photochemical reactivity involving any other reaction. If the donor is initially excited, competing reactions of the donor excited states must be considered.

(2) The lifetime of the excited state of the photosensitizer must be greater than the reciprocal of the rate of the electron-transfer process.

(3) The rate of the electron-transfer process can be predicted from the Weller equation (eq 1). The free energy change must be negative by at least 3 kcal mol⁻¹ in order for the electron-transfer process to be diffusion-controlled.

(4) Once the radical cation has formed, cleavage may occur if the bond dissociation energy, estimated by using eq 7, is less than about 15 kcal mol⁻¹. If the radical cation bond dissociation energy is too high, the cleavage reaction cannot compete with deactivation by back electron transfer.

(5) Radical cation cleavage requires a conformation that will allow orbital overlap at the transition state. Since the cleavage

process must be rapid in order to compete with back electron transfer, there may not be time for conformational change during the lifetime of the radical cation. Therefore, the preferred conformation of the donor must be favorable for cleavage. Orbital overlap must extend all the way from the SOMO of the radical cation site, through the α -carbon-carbon bond and through the anti-bonding σ -orbital of the α -carbon-carbon bond, to include the orbital that will provide stabilization for the incipient radical or cation.^{4b}

(6) The configuration of the SOMO is important; high spin and/or charge density on the ipso carbon is required.

(7) The regioselectivity of the radical cation cleavage depends upon the relative oxidation potentials of the fragment radicals. The fragment with the lower oxidation potential will react preferentially as the carbocation (eq 11).

(8) There is a good correlation between the oxidation potentials determined from the product ratio and the electrochemical data (eq 18).

(9) Formation of the hydrocarbon requires that the reduction potential of the radical be less than that of the photosensitizer. If this criterion is not met, the radical will be diverted to other products.

(10) The product ratio from cleavage of the radical cation at 25 °C can be used to calculate the difference in the oxidation potentials of the two possible radical fragments if the difference is <0.1 V (eq 11). These differences can then be used to establish the standard oxidation potentials of radicals referred to the diphenylmethyl radical (oxidation potential 0.350 V vs SCE) as the primary standard.

(11) The effect of temperature on the relative oxidation potentials of radicals is small (about 20 mV for a temperature change of 60 K) and is insignificant when the two radicals are of the same order (i.e., both secondary or both tertiary) and of similar size. The magnitude of the temperature effect is related to the entropy change for the electron exchange process between the radicals and carbocations involved.

(12) The standard oxidation potentials of substituted cumyl radicals correlate with Brown's σ^+ substituent constants with $\rho = -6$ (eq 19).

Experimental Section

General Information. The ¹H NMR spectra were recorded on a Varian EM360 NMR spectrometer and are reported in parts per million (ppm) downfield from TMS. Mass spectra (MS) were recorded on a Hewlett-Packard GC/MS system with 5970 Series Quadrupole Mass Selective Detector and are reported in m/z (rel intensity). Melting points (mp) were determined by using a Cybron Corporation Thermolyne melting point apparatus equipped with a calibrated Omega DP280 Series digital thermometer. Elemental analyses were performed by Canadian Microanalytical Service Ltd., Vancouver, BC and are reported for all new compounds. The acetonitrile used for the irradiations and electrochemical measurements was distilled successively from sodium hydride and phosphorus pentoxide, passed through a column of basic alumina, then refluxed with calcium hydride, and distilled under nitrogen. Methanol was dried by refluxing over magnesium followed by fractionation in an apparatus protected from moisture. Silica gel for flash chromatography was SILICAR 200-425 mesh Type 60A (Mallinckrodt). Solvents used for the flash chromatography were doubly distilled before use. Preparative medium-pressure liquid chromatography (MPLC) was carried out with use of a 2.5 cm \times 1 m column packed with TLC grade silica gel (without binder) (Merck 60PF-254) at 15 psi (helium).

Irradiation Procedure. The photosensitized (electron transfer) cleavage reaction was carried out in acetonitrile-methanol (3:1) solution at a substrate concentration of 0.10 M and a photosensitizer concentration of 0.02 M unless otherwise noted. The solutions were placed in 4-mm internal diameter Pyrex tubes (about 1-mL capacity), equipped with a gas-tight Teflon seal with a rubber septum for needle insertion. Before sealing, the solution was degassed by nitrogen ebullition. A Hanovia 450 W medium pressure mercury vapor lamp was used as the irradiation source. The lamp was equipped with a quartz cooling jacket and was surrounded by another Pyrex jacket with nests for six irradiation tubes. The temperature in the external jacket was thermostatically controlled by water circulation with a Julabo Model F10V circulating water bath.

Every compound was irradiated at least twice at each temperature. The relative oxidation potentials were determined from the ratio of ethers at several temperatures based on eq 11. The standard oxidation poten-

(19) (a) Exner, O. In *Advances in Linear Free Energy Relationships*; Chapman, N. B., Shorter, J., Eds.; Plenum Press: London, 1972. (b) Okamoto, Y.; Inukai, T.; Brown, H. C. *J. Am. Chem. Soc.* **1958**, *80*, 4969. (c) Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1958**, *80*, 4979.

(20) Harrison, A. G.; Kebarle, P.; Lossing, F. P. *J. Am. Chem. Soc.* **1961**, *83*, 777.

tials of radicals were then calculated from the appropriate oxidation potential differences, linearly interpolated to 25 °C, and the accuracy was statistically evaluated. The standard deviations reported for these potentials (σ_{red}) are based on at least 10 data points.

Electrochemical Measurements. Oxidation potentials were measured by cyclic voltammetry in acetonitrile with tetra-*n*-butylammonium perchlorate (0.10 M) as electrolyte. The substrate concentrations were typically 0.002 M. The working electrode was a 1-mm diameter platinum sphere, the counter electrode was a platinum wire, and the reference electrode was a saturated calomel electrode (SCE), which was galvanically connected to the solution by a Luggin capillary. Before the measurement the solution was purged with dry nitrogen for 5 min. The voltammograms were indicative of irreversible oxidation processes, so the oxidation potentials were taken as 0.028 V before the anodic peak potential at 100 mV s⁻¹ sweep rate.²¹ Compounds (oxidation potential, V vs SCE): 1-(4-methylphenyl)-1,2,2-triphenylethane (**19**) (1.89), 1,1-bis(4-methylphenyl)-2,2-diphenylethane (**20**) (1.83), 1,1,2-tris(4-methylphenyl)-2-phenylethane (**21**) (1.82).

Analytical Methods. After irradiation, each sample was analyzed quantitatively on a Hewlett-Packard 5890A gas chromatograph equipped with a flame ionization detector. The column oven temperature program was optimized for every mixture analyzed. In most cases it involved a 1.5-min isothermal period at 45 °C (solvent delay), followed by a linear temperature ramp of 20° min⁻¹ up to 280 °C, and then an additional isothermal period until all mixture components were eluted (total analysis time about 30 min per run). The column applied in most cases was OV-1701 (Supelco Ltd.), which was a 30-m, wide bore, fused silica capillary column covered with methyl (with 5% phenyl) silicone bonded to the capillary walls. Hydrogen was used as the carrier gas. Peak areas were integrated electronically by using a Hewlett-Packard 3392A integrator interfaced to a microcomputer, which acquired and stored digital data for later retrieval. The integration scan rate was 20 scan s⁻¹, which afforded about 25 scans per normal peak width.

The relative concentration of each of the cleavage products was based on peak areas and effective number of carbons in each product. For the hydrocarbon components the effective number of carbons was assumed to be equal to the number of carbons in the molecule. The effective number of carbons for the main cleavage products containing heteroatoms were found experimentally relative to the major hydrocarbon product. The average from several injections of a standard solution of known relative concentration of each of the components was used for this determination. The effective number of carbons for side products were calculated based on the number of carbons and increments for the heteroatoms involved in their structure. The increments were found experimentally by measurement of relative peak areas for some standard compounds containing the same number and type of heteroatom. The extent of conversion to the cleavage products was calculated from the material balance by using the concentration of 1,4-dicyanobenzene (**2**) (and the adduct) as the internal standard.

Preparation of Compounds. Samples of **12**, **14**, **16**, **20**, **24**, **25**, and **57** were available from previous work.⁴ The cleavage products **3**, **37**, **40**, **41**, **42**, **54**, **61**, **62**, **66**, and **68** were commercially available. The cleavage products **36**, **38**, **39**, **43**, **44**, **47**, **48**, **49**, **50**, **51**, **53**, **58**, **65**, **69**, **70**, and **71** were identified on the basis of GC/MS (retention time and characteristic mass spectral fragmentation patterns).

1-(4-Methylphenyl)-1,2,2-triphenylethane (19). A solution of 1-(4-methylphenyl)-1,2,2-triphenylethylene (2.4 g, 7 mmol) in cyclohexane (50 mL) was stirred with 5% Pd/C catalyst (2.0 g) under hydrogen (780 Torr) at room temperature until reduction was complete (3 days). Progress of the reaction was monitored by GC/MS. The catalyst was filtered off, and **19** was separated from traces of the alkene by MPLC. Pure **19** was obtained by crystallization from methanol: yield 1.48 g (61%), mp 145.5 °C; ¹H NMR (60 MHz, CDCl₃) δ 2.17 (s, 3 H, CH₃), 4.75 (s, 2 H, CHCH), 6.9–7.2 (m, 19 H, arom); MS, *m/z* (rel intensity) 182 (14), 181 (100), 167 (16), 166 (25), 165 (32), 152 (8). Anal. Calcd for C₂₇H₂₄: C, 93.06; H, 6.94. Found: C, 92.98; H, 6.99.

1-(4-Methylphenyl)-1,2,2-triphenylethylene. A solution of 1-(4-methylphenyl)-1,2,2-triphenylethanol (3.0 g) and 4-toluenesulfonyl chloride (0.3 g) in benzene (60 mL) was refluxed for 0.5 h. The solution was washed with 5% aqueous NaOH and dried over MgSO₄, and the solvent was evaporated. 1-(4-Methylphenyl)-1,2,2-triphenylethylene was isolated from the reaction mixture by flash chromatography with *n*-hexane/dichloromethane (9:1) as eluent: yield 2.4 g (84%); MS *m/z* (rel intensity) 346 (M⁺, 100), 347 (M⁺ + 1, 31), 253 (25), 252 (17).

1-(4-Methylphenyl)-1,2,2-triphenylethanol. A suspension of 1,2,2-triphenylethanol (13.5 g, 0.05 mol) in diethyl ether (125 mL) was added dropwise to a solution of (4-methylphenyl)magnesium bromide which was prepared from 4-bromotoluene (16.5 g, 0.13 mol) and magnesium (3.2

g, 0.13 g atom) in diethyl ether (50 mL). The resulting mixture was refluxed for 45 min, then cooled, and poured onto a mixture of NH₄Cl (20 g) and ice (100 g). The organic layer was separated, and the aqueous layer was extracted with dichloromethane. The solvent was removed from the combined extract to yield the crude product (18.5 g) as a mixture which contained about 25% of the desired alcohol and 75% of unreacted ketone (by ¹H NMR). The starting material was extracted from the product with hot ethanol and the product obtained by recrystallization from ethanol: ¹H NMR (60 MHz, CDCl₃) δ 2.23 (s, 3 H, CH₃), 2.78 (s, 1 H, OH), 5.24 (s, 1 H, CH), 7.0–7.3 (m, 19 H, arom).

1,2,2-Triphenylethanol. A solution of desyl chloride²² (25 g, 0.108 mol) in benzene (50 mL) was added dropwise to the suspension of AlCl₃ (16 g, 0.12 mol) in benzene (75 mL) within 10 min. The mixture was refluxed for 0.5 h, then cooled, and poured onto ice (100 g) and concentrated HCl (20 mL). The organic layer was separated and dried with anhydrous MgSO₄, and the solvent was evaporated. The crude reaction mixture was crystallized from ethanol giving 1,2,2-triphenylethanol (18.6 g, 84%): mp 138–139 °C (lit.²³ mp 139 °C); ¹H NMR (60 MHz, CDCl₃) δ 6.03 (s, 1 H, CH), 7.2–7.5 (m, 13 H, arom), 8.00 (m, 2 H, o-aryl); MS *m/z* (rel intensity) 167 (40), 165 (30), 152 (15.5), 105 (100), 77 (47), 51 (18).

1,1,2-Tris(4-methylphenyl)-2-phenylethane (21). Catalytic hydrogenation of 1,1,2-tris(4-methylphenyl)-2-phenylethylene (2.5 g, 9.1 mmol) by the method described above for the preparation of 1-(4-methylphenyl)-1,2,2-triphenylethane gave this alkane (1.9 g, 75%) which was purified by recrystallization from ethanol/acetone: mp 219 °C; ¹H NMR (60 MHz, CDCl₃) δ 2.14 (s, 9 H, CH₃), 4.68 (s, 2 H, CH), 6.8–7.2 (m, 17 H, arom); MS *m/z* (rel intensity) 195 (100), 181 (22), 180 (10), 165 (35). Anal. Calcd for C₂₉H₂₈: C, 92.50; H, 7.50. Found: C, 92.57; H, 7.52.

2-Hydroxy-1,2-bis(4-methylphenyl)ethanone (4-Toluoino). An aqueous solution of KCN (30%, 100 mL) was added dropwise to the stirred solution of freshly distilled 4-methylbenzaldehyde (234 g, 1.95 mol) in aqueous ethanol (300 mL in 140 mL water). The mixture was refluxed for 4 h under nitrogen, then cooled, and diluted with water (100 mL). The organic products were extracted with dichloromethane (300 mL), the extract was washed with aqueous NaCl (5%), and the solvent and unreacted 4-methylbenzaldehyde were distilled off under vacuum to yield crude 4-toluoino (152 g). Recrystallization from 95% ethanol gave a pure product (117 g, 50%): mp 89 °C (lit.²⁴ mp 87–88 °C); ¹H NMR (60 MHz, CDCl₃) δ 2.28, 2.33 (ds, 6 H, CH₃), 4.53 (d, 1 H, OH), 5.88 (d, 1 H, CH), 7.08–7.32 (m, 6 H, arom), 7.82 (d, 2 H, o-aryl).

2-Chloro-1,2-bis(4-methylphenyl)ethanone. Freshly distilled thionyl chloride (73 mL, 1.0 mol) was added to 1-hydroxy-1,2-bis(4-methylphenyl)ethanone (100 g, 0.42 mol). The mixture was stirred at room temperature (15 min) and was then refluxed (15 min), while HCl was given off. Excess SOCl₂ was distilled off under vacuum, and the product was dissolved in hexanes (100 mL). The solvent (and HCl) was distilled off under vacuum, the residue was dissolved in dichloromethane (100 mL), and the solvent (and HCl) was distilled off again. 2-Chloro-1,2-bis(4-methylphenyl)ethanone was obtained as an oil which was used for the next step without further purification: ¹H NMR (60 MHz, CDCl₃) δ 2.32, 2.38 (ds, 6 H, CH₃), 6.30 (s, 1 H, CH), 7.13–7.43 (m, 6 H, arom), 7.87 (d, 2 H, o-aryl).

1,2,2-Tris(4-methylphenyl)ethanone. 2-Chloro-1,2-bis(4-methylphenyl)ethanone (100 g, 0.386 mol) was dissolved in toluene (600 mL), and AlCl₃ (57 g, 0.42 mol) was added in portions over 15 min. The mixture was stirred for 2.5 h at room temperature, while HCl was released. Then the mixture was heated under reflux for 0.5 h, cooled to room temperature, and was poured onto a mixture of concentrated HCl (50 mL) and ice (200 g). The organic layer was separated, refluxed for 15 min with decolorizing charcoal, dried over anhydrous MgSO₄, and filtered. The solvent was evaporated to yield the crude product as an oil (113 g, containing about 20% 4,4'-dimethylbenzil as the major impurity). 1,2,2-Tris(4-methylphenyl)ethanone was purified by vacuum distillation, obtained in the fraction boiling at 205–207 °C/0.05 Torr (4,4'-dimethylbenzil distilled first at 181–185 °C/0.03 Torr). The distillate contained 1,2,2-tris(4-methylphenyl)ethanone of sufficient purity (>97%) for the next step. The impurity (about 2%) was a mixture of other isomers, presumably 2-methyl substituted in one of the aromatic rings: yield 85 g (70%). An analytical sample was prepared by recrystallization from *n*-hexane: mp 85–85.5 °C (lit.²⁵ mp 88 °C); ¹H NMR (60 MHz, CDCl₃) δ 2.32 (s, 6 H, 2CH₃), 2.35 (s, 3 H, CH₃), 5.98 (s, 1 H, CH),

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7.17–7.28 (m, 10 H, arom), 7.95 (d, 2 H, arom, $J = 8$ Hz); MS m/z (rel intensity) 312 (13), 195 (66), 180 (10), 178 (8), 165 (17), 119 (100), 91 (26), 65 (10).

1-Phenyl-1,2,2-tris(4-methylphenyl)ethanol. The addition of phenylmagnesium bromide to 1,2,2-tris(4-methylphenyl)ethanone, by using the procedure described above for the preparation of 1-(4-methylphenyl)-1,2,2-triphenylethanol, gave this alcohol in low (14%) yield. This crude product was used directly in the dehydration procedure described below.

1,1,2-Tris(4-methylphenyl)-2-phenylethylene. The mixture (68.8 g) of 1-phenyl-1,2,2-tris(4-methylphenyl)ethanol (14%) and 1,2,2-tris(4-methylphenyl)ethanone (86%) from the Grignard reaction described above and 4-toluenesulfonic acid (1.0 g), acetyl chloride (20 mL), and benzene (100 mL) were refluxed for 3.5 h, then cooled, and poured into water (200 mL). The mixture was extracted with dichloromethane (200 mL). The extract was washed with aqueous K_2CO_3 (5%) and dried over anhydrous $MgSO_4$, and then the solvent was evaporated. The crude mixture (68.0 g) was separated by flash chromatography with *n*-hexane/dichloromethane (9:1) as eluent: 1,1,2-tris(4-methylphenyl)-2-phenylethylene (7.2 g, 9.9% yield based on the amount of 1,2,2-tris(4-methylphenyl)ethanone used for the Grignard reaction). The ketone (50 g, 81%) was recovered. The 1,1,2-tris(4-methylphenyl)-2-phenylethylene isolated was 96.5% pure (3.5% other isomers). Crystallization successively from methanol/acetone, acetone/pentanes, and finally methanol/acetone gave pure 1,1,2-tris(4-methylphenyl)-2-phenylethylene (3.02 g, >99.8% purity by GC/FID): mp 139.5–140 °C; 1H NMR (60 MHz, $CDCl_3$) δ 2.25 (s, 9 H, 3 CH_3), 6.93 (s, 12 H, arom), 7.07 (s, 5 H, C_6H_5); MS m/z (rel intensity) 374 (M^+ , 100), 375 ($M^+ + 1$, 29.1). Anal. Calcd for $C_{25}H_{26}$: C, 93.00; H, 7.00. Found: C, 92.98; H, 6.99.

(4-Methylphenyl)phenylmethane (32). A solution of $AlCl_3$ (106.7 g, 0.8 mol) in diethyl ether (200 mL) was added slowly to a stirred slurry of $LiAlH_4$ (15.2 g, 0.4 mol) in ether (100 mL), and the mixture was stirred for 5 min. A solution of 4-methylbenzophenone (49.1 g, 0.25 mol) was then added dropwise, while the reaction mixture was stirred. The exothermic reaction kept the mixture refluxing. When the refluxing stopped, the mixture was stirred for another 15 min, and ethyl acetate (53 mL, 0.55 mol) was added dropwise to decompose excess reagent. The mixture was poured onto ice (300 g) and NH_4Cl (85 g), and the ethereal layer was separated and washed with saturated sodium chloride solution (100 mL). The aqueous layer was extracted with dichloromethane (2 \times 100 mL), the extracts were combined with the ether solution and dried with $MgSO_4$, and the solvent was evaporated. The crude product was distilled under vacuum (bp 112 °C/0.05 Torr) to yield pure **32** as a colorless liquid (42.9 g, 94%): 1H NMR (60 MHz, $CDCl_3$) δ 2.31 (s, 3 H, CH_3), 3.95 (s, 2 H, CH_2), 7.10 (s, 4 H, arom), 7.23 (m, 5 H, arom); MS m/z (rel intensity) 182 (M^+ , 74), 181 (18), 167 (100), 166 (24), 165 (47), 152 (18), 91 (10).

Bis(4-methylphenyl)methane (34). This compound was prepared (82% yield) from 4,4'-dimethylbenzhydrol following the same procedure as that which was used for the preparation of **32** described above: bp 115 °C/0.10 Torr; 1H NMR (60 MHz, $CDCl_3$) δ 2.32 (s, 6 H, 2 CH_3), 3.92 (s, 2 H, CH_2), 7.13 (s, 8 H, arom); MS m/z (rel intensity) 196 (M^+ , 58), 181 (100), 179 (10), 178 (13), 166 (31), 165 (32), 104 (13), 77 (13).

Methyl Diphenylmethyl Ether (5). A solution of benzhydrol chloride (22 mL, 0.124 mol) and sodium methoxide (13.5 g, 0.25 mol) in anhydrous methanol (50 mL) was refluxed for 7 h and was then stirred at room temperature overnight. The solution was diluted with water (50 mL), the product was extracted with dichloromethane (2 \times 50 mL) and dried with $MgSO_4$, and the solvent was evaporated to yield **5** (23.0 g, 98% purity). The major impurity (benzophenone) was not separated by vacuum distillation. The ketone in the mixture was reduced with $LiAlH_4$ in ether, and the resulting alcohol was converted to the ether **5** with NaH and Me_2SO_4 . The solvent was evaporated, and the residue was vacuum distilled. Pure **5** was obtained: bp 116–117 °C/0.3 Torr; MS m/z (rel intensity) 198 (M^+ , 58), 197 (16), 167 (76), 165 (47), 152 (20), 121 (100), 105 (62), 91 (30), 77 (76), 63 (15), 51 (38).

Methyl (4-Methylphenyl)phenylmethyl Ether (33). This ether was obtained from 4-methylbenzhydrol chloride and sodium methoxide according to the procedure described above for **5**. The small sample of methyl (4-methylphenyl)phenylmethyl ether (**33**) needed as a standard was purified by preparative gas chromatography: MS m/z (rel intensity) 212 (M^+ , 78), 198 (32), 181 (100), 166 (50), 165 (59), 152 (15), 135 (61), 121 (28), 119 (57), 105 (54), 91 (46), 77 (49), 65 (20), 51 (31).

Methyl Bis(4-methylphenyl)methyl Ether (35). This compound was prepared from 4,4'-dimethylbenzhydrol chloride by using the procedure described above for **5**. The small sample needed for the standard solution was purified by preparative gas chromatography: MS m/z (rel intensity) 226 (M^+ , 54), 211 (30), 196 (34), 195 (100), 181 (45), 180 (27), 178 (22), 165 (44), 135 (44), 119 (53), 91 (32), 65 (13).

4-Methylbenzhydrol (55). This alcohol was prepared by the Grignard reaction of (4-methylphenyl)magnesium bromide and benzaldehyde.

Details of the procedure were similar to those used for the preparation of 4,4'-dimethylbenzhydrol described below: MS m/z (rel intensity) 198 (M^+ , 34), 183 (23), 165 (13), 119 (79), 105 (100), 91 (37), 77 (36), 65 (12), 51 (16).

4,4'-Dimethylbenzhydrol (59). The solution of 4-tolualdehyde (59.0 g, 0.50 mol) in dry diethyl ether (100 mL) was added dropwise to the stirred solution of (4-methylphenyl)magnesium bromide prepared from 4-bromotoluene (61.5 mL, 0.50 mol) and magnesium (12.2 g, 0.50 g atom) in ether (200 mL). After all the aldehyde had been added, the mixture was stirred for 0.5 h and was then poured onto a mixture of NH_4Cl (50 g) and ice (300 g). The product was extracted with dichloromethane (400 mL), which was then dried with anhydrous $MgSO_4$, and evaporated to yield crude product (104.9 g). Recrystallization of this crude material from *n*-hexane gave **59** (60.7 g, 57.2%): mp 68–69 °C; 1H NMR (60 MHz, $CDCl_3$) δ 2.25 (br s, 1 H, OH), 2.32 (s, 6 H, 2 CH_3), 5.76 (s, 1 H, CH), 7.05–7.37 (dd, 8 H, arom); MS m/z (rel intensity) 212 (M^+ , 25), 197 (20), 165 (10), 121 (21), 119 (100), 105 (23), 91 (49), 77 (20), 65 (23).

2-Methyl-1-(4-methylphenyl)-1,2-diphenylpropane (29). Potassium (1.67 g, 0.043 g atom), in small pieces, was added to liquid ammonia (100 mL) and anhydrous $FeCl_3$ (20 mg) in a flask with a dry ice/acetone cooled upright condenser and a drying tube. The solution was stirred until the deep blue color disappeared (about 0.5 h). Then a solution of (4-methylphenyl)phenylmethane (**32**) (7.8 g, 43 mmol) in diethyl ether (25 mL) was added dropwise over 15 min, and the mixture was stirred for another 15 min. The brown-red color of the (4-methylphenyl)phenylmethyl carbanion formed at this stage. Next, 2-bromo-2-phenylpropane (8.5 g, 43 mmol) in diethyl ether (35 mL) was added dropwise over 10 min, the dry ice condenser was changed to an air condenser, and the mixture was stirred overnight while the ammonia evaporated. The residue was diluted with water (100 mL), and the product was extracted into dichloromethane (50 mL). The extract was washed with saturated salt solution (50 mL) and dried with $MgSO_4$, and the solvents were evaporated. The crude product was vacuum distilled, and a fraction boiling at 165–175 °C/0.025 Torr was collected (3.9 g, 30%, >97% purity). The distillate was further purified by flash chromatography with use of *n*-hexane/dichloromethane (9:1) to yield pure **29** (3.3 g) as a viscous liquid: 1H NMR (60 MHz, $CDCl_3$) δ 1.42 (s, 6 H, 2 CH_3), 2.25 (s, 3 H, CH_3), 4.16 (s, 1 H, CH), 7.02 (s, 4 H, arom), 7.15 and 7.18 (br s, 10 H, 2Ph); MS m/z (rel intensity) 181 (100), 166 (23), 165 (29), 119 (25), 118 (17), 103 (11), 91 (24), 77 (12), 51 (10). Anal. Calcd for $C_{23}H_{24}$: C, 91.95; H, 8.05. Found: C, 92.14; H, 8.02.

2-Methyl-1,1-bis(4-methylphenyl)-2-phenylpropane (30). This compound was obtained by coupling the anion of bis(4-methylphenyl)methane with 2-bromo-2-phenylpropane. The procedure was similar to that described above for the preparation of **29**. Flash chromatography gave pure **30** (51%) as a viscous liquid: 1H NMR (60 MHz, $CDCl_3$) δ 1.58 (s, 6 H, 2 CH_3), 2.25 (s, 6 H, 2 CH_3), 4.10 (s, 1 H, CH), 7.02 (s, 8 H, arom), 7.18 (s, 5 H, arom); MS m/z (rel intensity) 195 (100), 180 (22), 179 (17), 178 (13), 165 (38), 119 (13), 118 (12), 117 (13), 103 (10), 91 (22), 77 (10). Anal. Calcd for $C_{24}H_{26}$: C, 91.67; H, 8.33. Found: C, 91.75; H, 8.28.

1,1,2,2-Tetrakis(4-methylphenyl)ethane (**57**) was isolated as a side product: 1H NMR (60 MHz, $CDCl_3$) δ 2.17 (s, 12 H, 4 CH_3), 4.68 (s, 2 H, CHCH), 6.87 and 7.08 (dd, 16 H, arom); MS m/z (rel intensity) 195 (100), 180 (16), 179 (11), 178 (10), 165 (22), 119 (11).

2-(4-Fluorophenyl)-2-methyl-1-(4-methylphenyl)-1-phenylpropane (26). Coupling the anion of (4-methylphenyl)phenylmethane with 2-bromo-2-(4-fluorophenyl)propane, by using the procedure described above for the synthesis of **29**, gave **26**. Purification by flash chromatography and recrystallization from ethanol gave pure **26** (48%): mp 80.5 °C; 1H NMR (60 MHz, $CDCl_3$) δ 1.40 (s, 6 H, 2 CH_3), 2.27 (s, 3 H, CH_3), 4.08 (s, 1 H, CH), 6.7–7.4 (m, 13 H, arom); MS m/z (rel intensity) 181 (100), 166 (23), 165 (26), 137 (21), 136 (26), 135 (15), 121 (18), 109 (23), 101 (15). Anal. Calcd for $C_{23}H_{23}F$: C, 86.75; H, 7.28. Found: C, 86.96; H, 7.34.

2-(4-Fluorophenyl)-2-methyl-1,1-bis(4-methylphenyl)propane (27). Reaction of the anion of bis(4-methylphenyl)methane (**34**) with 2-bromo-2-(4-fluorophenyl)propane, as described above for the preparation of **29**, gave **27** which was purified by flash chromatography. A 30% yield of **27** (viscous liquid) was obtained: 1H NMR (60 MHz, $CDCl_3$) δ 1.38 (s, 6 H, 2 CH_3), 2.24 (s, 6 H, 2 CH_3), 4.02 (s, 1 H, CH), 6.67–7.17 (m, 12 H, arom); MS m/z (rel intensity) 195 (100), 180 (20), 179 (13), 178 (12), 165 (28), 136 (25), 135 (19), 121 (19), 109 (18), 101 (13). Anal. Calcd for $C_{24}H_{25}F$: C, 86.70; H, 7.58. Found: C, 86.39; H, 7.47.

2-Methyl-1,1,2-tris(4-methylphenyl)propane (31). This alkane was synthesized from bis(4-methylphenyl)methane (**34**) and 2-bromo-2-(4-methylphenyl)propane as described above for **29**. Pure **31** (41%) was obtained by flash chromatography as a colorless viscous liquid: 1H NMR (60 MHz, $CDCl_3$) δ 1.39 (s, 6 H, 2 CH_3), 2.26 (s, 6 H, 2 CH_3), 2.31 (s,

3 H, CH₃), 4.10 (s, 1 H, CH), 7.02 and 7.05 (ds, 12 H, arom); MS *m/z* (rel intensity) 195 (100), 180 (12), 179 (11), 178 (11), 165 (23), 133 (50), 132 (20), 117 (23), 115 (13), 105 (21), 91 (20). Anal. Calcd for C₂₅H₂₈: C, 91.41; H, 8.59. Found: C, 91.62; H, 8.63.

1,1,2-Triphenylpropane (23). Coupling of the anion of diphenylethane (3) with 1-bromo-1-phenylethane according to the procedure described for 29, gave 23 (24%) which was purified by flash chromatography and recrystallization from ethanol: mp 73 °C (lit.²⁶ mp 73–5 °C); ¹H NMR (60 MHz, CDCl₃) δ 1.20 (d, 3 H, CH₃), 3.32–4.18 (m, 2 H, CHCH), 7.08–7.45 (m, 15 H, 3Ph); MS *m/z* (rel intensity) 272 (M⁺, <1), 167 (100), 165 (22), 152 (12), 105 (12).

2,2,3-Triphenylbutane (28). Coupling of the anion of 1,1-diphenylethane (60) with 1-bromo-1-phenylethane, as described above, gave 28 (45%). The pure material was obtained by successive flash chromatography, first by using *n*-hexane/dichloromethane (1:1) and again by using *n*-hexane as the eluent: ¹H NMR (60 MHz, CDCl₃) δ 1.34 (d, 3 H, CH₃), 1.50 (s, 3 H, CH₃), 3.80 (q, 1 H, CH), 6.6–7.2 (m, 15 H, 3Ph); MS *m/z* (rel intensity) 182 (66), 181 (100), 179 (25), 178 (24), 166 (67), 165 (79), 105 (22), 104 (20), 103 (98), 77 (80), 51 (24). Anal. Calcd for C₂₂H₂₂: C, 92.26; H, 7.74. Found: C, 92.30; H, 7.83.

1,1,2,2-Tetraphenylethane (22). This compound was obtained by coupling the anion of 1,1-diphenylethane (60) with benzhydryl chloride as described above. The crude product was first crystallized from ethanol (95%) to give 22 contaminated with 1,1,2,2-tetraphenylethane and tetraphenylethylene. The tetraphenylethylene was separated by flash chromatography with use of *n*-hexane/dichloromethane (2.5:1) as the eluent, and the remaining two components were separated by medium pressure liquid chromatography (MPLC) by using a gradient of *n*-hexane and dichloromethane as eluent. Pure 22 was obtained in low (9%) yield: mp 148.5 °C dec; ¹H NMR (60 MHz, CDCl₃) δ 2.00 (s, 3 H, CH₃), 5.11 (s, 1 H, CH), 7.02–7.15 (m, 20 H, 4Ph). Anal. Calcd for C₂₇H₂₄: C, 93.06; H, 6.94. Found: C, 92.87; H, 6.95.

2-Bromo-2-phenylpropane. Dry hydrogen bromide was bubbled through a suspension of anhydrous MgSO₄ (24 g, 0.2 mol) in a solution of 2-phenyl-2-propanol (13.6 g, 0.1 mol) in petroleum ether (100 mL) for 0.5 h. The magnesium sulfate was filtered off, and the solvent was evaporated to yield the bromopropane (18.3 g, 92%): ¹H NMR (60 MHz, CDCl₃) δ 2.20 (s, 6 H, 2CH₃), 7.3–7.7 (m, 5 H, arom).

2-(4-Fluorophenyl)-2-propanol. A solution of 4-fluoroacetophenone (30.4 mL, 0.25 mol) in anhydrous diethyl ether (75 mL) was added dropwise to a stirred solution of methylmagnesium iodide prepared from magnesium (9.1 g, 0.375 g atom), methyl iodide (23.5 mL, 0.38 mol), and ether (100 mL). After the ketone had been added, the mixture was stirred for 0.5 h and was then poured onto a mixture of ice (200 g) and NH₄Cl (50 g). The product was isolated and purified as described for 2-(4-methylphenyl)-2-propanol. Pure 2-(4-fluorophenyl)-2-propanol (33.0 g, 86%) was obtained by fractional distillation: bp 66–68 °C/0.3 Torr; ¹H NMR (60 MHz, CDCl₃) δ 1.57 (s, 6 H, 2CH₃), 1.80 (s, 1 H, OH), 6.87–7.60 (m, 4 H, arom).

2-Bromo-2-(4-fluorophenyl)propane. This bromopropane was obtained (88%) from 2-(4-fluorophenyl)-2-propanol according to the procedure described above for the preparation of 2-bromo-2-phenylpropane: ¹H NMR (60 MHz, CDCl₃) δ 2.18 (s, 6 H, 2CH₃), 7.08 (q, 2 H, J_{H,H} = 9 Hz, J_{H,F} = 16 Hz, arom), 7.63 (q, 2 H, J_{H,H} = 9 Hz, J_{H,F} = 5 Hz, arom).

1,1-Diphenylethane (60). A solution of freshly distilled 1,1-diphenylethylene (13.7 g, 76 mmol) and hydrazine monohydrate (5 mL, 0.1 mol) in absolute ethanol (100 mL) was refluxed with 5% Pd/C catalyst (1.0 g). Another portion of NH₂NH₂·H₂O (5.5 mL) and palladium catalyst (0.5 g) was added, and the mixture was refluxed overnight. The catalyst was filtered off, the filtrate was poured into dilute HCl (100 mL), and the product was extracted with dichloromethane (150 mL), dried with MgSO₄, and vacuum distilled to afford 1,1-diphenylethane (9.3 g, 67%): bp 105–106 °C/0.5 Torr; ¹H NMR (60 MHz, CDCl₃) δ 1.63 (d, 3 H, CH₃), 4.18 (q, 1 H, CH), 7.27 (s, 10 H, 2Ph); MS *m/z* (rel intensity) 182 (M⁺, 28), 167 (100), 165 (31), 152 (19), 77 (21), 51 (16).

1-Bromo-1-phenylethane. To a stirred suspension of *N*-bromosuccinimide (35.6 g, 0.20 mol) (recrystallized from water and dried in a desiccator) in freshly distilled carbon tetrachloride (150 mL) was added ethylbenzene (27 mL, 0.22 mol) and benzoyl peroxide (0.5 g). The mixture was briefly heated to initiate reaction. Following an exothermic reaction, the mixture was heated under reflux for another 0.5 h and then cooled to room temperature, and the fluffy white solid (succinimide) was filtered off. Carbon tetrachloride was evaporated, and the crude product was fractionated under vacuum. A fraction boiling at 81 °C/2 Torr (24.8 g, 67%) was collected: ¹H NMR (60 MHz, CDCl₃) δ 2.04 (d, CH₃), 5.21 (q, 1 H, CH), 7.22–7.48 (m, 5 H, arom).

2-(4-Methylphenyl)-2-propanol. A solution of ethyl 4-methylbenzoate (41.0 g, 0.25 mol) in dry diethyl ether (75 mL) was added dropwise to an excess of methylmagnesium iodide solution prepared from magnesium

(18.2 g, 0.75 g atom), methyl iodide (46.7 mL, 0.75 mol), and ether (200 mL). The rate of the addition was maintained such as to keep the mixture refluxing from the heat of reaction. The mixture was poured on ice (200 g) and NH₄Cl (50 g), and the ether layer was separated. The aqueous phase was extracted with dichloromethane (100 mL), the combined extract was dried with MgSO₄ and the solvent was evaporated. The crude product was vacuum distilled at 80 °C/0.15 Torr to yield pure 2-(4-methylphenyl)-2-propanol (28.3 g, 75%): ¹H NMR (60 MHz, CDCl₃) δ 1.58 (s, 6 H, 2CH₃), 1.73 (s, 1 H, OH), 2.35 (s, 3 H, CH₃), 7.17, 7.44 (dd, 2 H, arom); MS *m/z* (rel intensity) 150 (M⁺, 5), 135 (48), 132 (100), 117 (100), 115 (81), 105 (9), 92 (33), 91 (80), 77 (19), 65 (45), 63 (26), 51 (29).

2-Bromo-2-(4-methylphenyl)propane. This compound was obtained (91%) from 2-(4-methylphenyl)-2-propanol by the procedure described above for the preparation of 2-bromo-2-phenylpropane: ¹H NMR (60 MHz, CDCl₃) δ 2.19 (s, 6 H, 2CH₃), 2.34 (s, 3 H, CH₃), 7.17 (d, 2 H, J = 9 Hz, arom), 7.56 (d, 2 H, J = 9 Hz, arom).

4-Cyanocumene (45). A mixture of 4-iodocumene (12.8 g, 52 mmol), anhydrous cuprous cyanide (7.0 g, 78 mmol), copper powder (0.33 g, 5 g atom), and dry pyridine (50 mL) was refluxed for 3 days. The mixture was poured into aqueous ammonia (300 mL, 10%), and the product was extracted with dichloromethane (100 mL). The extract was filtered through a Celite pad, washed with HCl (100 mL, 10%) containing H₂O₂ (3 mL, 30%) and then washed with aqueous NaHSO₃ solution (100 mL), and dried with MgSO₄, and the solvent was evaporated. The crude product was diluted with *n*-hexane and the side product, 4-isopropylbenzamide, was filtered off. The hexane was removed on a rotary evaporator, and the residue was vacuum distilled (bp 85 °C/0.7 Torr) to give impure 4-cyanocumene (3.4 g, 45% yield, 97.5% purity). The pure sample of 4-cyanocumene needed as a standard was obtained by further purification by using preparative gas chromatography (column: SE-30 on Chromosorb W): MS *m/z* (rel intensity) 145 (M⁺, 22), 130 (100), 103 (27), 77 (12).

4-Cyanocumyl Methyl Ether (46). The alcohol, 2-(4-cyanophenyl)-2-propanol, was converted to the ether with dimethyl sulfate as described below for the preparation of methyl 4-(trifluoromethyl)cumyl ether. In this case, however, 2-(4-cyanophenyl)propene was formed as a side product. Therefore, the crude reaction mixture was partially separated by flash chromatography, by using dichloromethane/hexane (1:1) as the eluent. A small sample of 4-cyanocumyl methyl ether needed as a standard was purified by preparative gas chromatography (column: 10% diethylene glycol succinate on Chromosorb P): MS *m/z* (rel intensity) 175 (M⁺, <0.5), 160 (100), 144 (13), 116 (23), 102 (11).

4-(Trifluoromethyl)cumene (18). A solution of 2-[4-(trifluoromethyl)phenyl]propene (6.3 g, 34 mmol) in cyclohexane (30 mL) was stirred under hydrogen with Pd/C catalyst (1.0 g, 5%) at room temperature and atmospheric pressure for 3 h. The catalyst was filtered off, and the solvent was removed on a rotary evaporator. The residue was vacuum distilled at 40 °C/0.95 Torr to afford pure 4-(trifluoromethyl)cumene (4.4 g, 69%): ¹H NMR (60 MHz, CDCl₃) δ 1.26 (d, 6 H, 2CH₃), 2.98 (sept, 1 H, CH), 7.35 and 7.59 (dd, 4 H, arom); MS *m/z* (rel intensity) 188 (M⁺, 28), 173 (100), 169 (13), 153 (28), 133 (55), 127 (14), 119 (21).

Methyl 4-(Trifluoromethyl)cumyl Ether (17). A 50% dispersion of sodium hydride in mineral oil (3.9 g, 0.08 mol NaH) was washed with *n*-hexane (3 × 50 mL), and the residue (NaH) was transferred to a solution of 2-[4-(trifluoromethyl)phenyl]-2-propanol (8.3 g, 41 mmol) in dry diethyl ether (50 mL). The slurry was stirred for 10 min, dimethyl sulfate (5.8 mL, 60 mmol) was added, and the mixture was refluxed overnight. The reaction mixture was poured into aqueous ammonia (200 mL, 15%), the product was extracted with dichloromethane (2 × 75 mL), and the extract was shaken with concentrated aqueous ammonium hydroxide (50 mL) for 15 min to remove excess dimethyl sulfate. The solvent was evaporated, and the crude product was vacuum distilled at 51 °C/0.5 Torr to afford pure methyl 4-(trifluoromethyl)cumyl ether (17) (6.9 g, 77%): ¹H NMR (60 MHz, CDCl₃) δ 1.53 (s, 6 H, 2CH₃), 3.10 (s, 3 H, OCH₃), 7.60 (s, 4 H, arom); MS *m/z* (rel intensity) 218 (M⁺, 0.5), 203 (100), 187 (15), 186 (22), 159 (23), 151 (15), 145 (12), 117 (24), 115 (15), 73 (13), 43 (57), 41 (18).

Cumyl Methyl Ether (15). Alkylation of 2-phenyl-2-propanol with dimethyl sulfate, according to the procedure described above for the preparation of methyl 4-(trifluoromethyl)cumyl ether, gave cumyl methyl ether: MS *m/z* (rel intensity) 150 (M⁺, 1), 135 (100), 118 (39), 117 (34), 103 (26), 91 (34), 78 (20), 77 (33), 51 (25), 43 (52).

2,3-Dimethyl-2,3-diphenylbutane (Dicumyl) (63). A solution of 2-bromo-2-phenylpropane (10.0 g, 50 mmol) in anhydrous diethyl ether (25 mL) was stirred with magnesium turnings (0.60 g, 0.025 g atom) overnight. The reaction mixture was poured into aqueous NH₄Cl solution (100 mL, 5%) and extracted with dichloromethane (100 mL). The solvent was evaporated, and the solid residue was recrystallized from 95%

ethanol to give 2,3-dimethyl-2,3-diphenylbutane (**63**) (2.4 g, 47%): $^1\text{H NMR}$ (60 MHz, CDCl_3) δ 1.32 (s, 12 H, 4 CH_3), 7.15 (s, 5 H, arom); MS m/z (rel intensity) 119 (100), 118 (26), 117 (18), 103 (16), 91 (50), 78 (12), 77 (16).

2-[4-(Trifluoromethyl)phenyl]-2-propanol. This alcohol was prepared by the addition of methylmagnesium iodide to 4-(trifluoromethyl)acetophenone according to the procedure described for the preparation of 2-(4-methylphenyl)-2-propanol. 2-[4-(Trifluoromethyl)phenyl]-2-propanol (81%) was isolated by distillation: bp 84 °C/1.1 Torr; $^1\text{H NMR}$ (60 MHz, CDCl_3) δ 1.57 (s, 6 H, 2 CH_3), 2.48 (brd q, 1 H, OH), 7.57 (s, 4 H, arom); MS m/z (rel intensity) 204 (M^+ , 1), 189 (49), 186 (47), 151 (20), 145 (12), 117 (48), 115 (23), 43 (100).

2-(4-Cyanophenyl)-2-propanol. A solution of methylmagnesium iodide prepared from methyl iodide (3.8 mL, 60 mmol), magnesium (1.45 g, 0.060 g atom), and dry diethyl ether (20 mL) was added dropwise to an ether solution of 4-cyanoacetophenone (7.3 g, 50 mmol). The mixture was stirred for 0.5 h and was then poured into aqueous saturated NH_4Cl solution (200 mL). The product was extracted with dichloromethane (2 \times 100 mL) and dried with MgSO_4 , and the solvent was evaporated. Analysis (GC/MS) of the extract indicated that the conversion of 4-cyanoacetophenone to the alcohol was not complete. A significant amount of 4-cyanoacetophenone remained; however, no addition to the cyano group was observed under these conditions. The 2-(4-cyanophenyl)-2-propanol was partially separated by flash chromatography by using dichloromethane as eluent. The enriched fractions were combined, and the product was distilled under vacuum (bp 115–118 °C/0.2 Torr)

to give 2-(4-cyanophenyl)-2-propanol (5.0 g, >96% purity) still contaminated with the starting ketone: MS m/z (rel intensity) 161 (M^+ , 1), 146 (51), 43 (100).

2-(4-(Trifluoromethyl)phenyl)propene. A sodium hydride dispersion (3.8 g, 80 mmol, 50% NaH) in mineral oil was washed with *n*-hexane (3 \times 20 mL), and the clean NaH residue was added to a solution of methyl triphenylphosphonium bromide (25.7 g, 72 mmol) in anhydrous diethyl ether (100 mL). The mixture was refluxed under argon for 3 h, then 4-(trifluoromethyl)acetophenone (9.4 g, 50 mmol) in diethyl ether (25 mL) was added, and the solution was refluxed overnight. The reaction mixture was poured into water (200 mL), extracted with dichloromethane (2 \times 75 mL), and dried with magnesium sulfate, and the solvent was evaporated. The crude mixture was vacuum distilled at 53 °C/0.8 Torr to afford pure 2-(4-trifluoromethylphenyl)propene (6.3 g, 68%): $^1\text{H NMR}$ (60 MHz, CDCl_3) δ 2.18 (d, 3 H, CH_3), 5.22 (m, 1 H, = CH_A), 5.45 (m, 1 H, = CH_B), 7.58 (s, 4 H, arom); MS m/z (rel intensity) 186 (M^+ , 100), 171 (24), 167 (21), 151 (47), 146 (17), 117 (100), 115 (50).

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Cis-Trans Photoisomerization of a *p*-Styrylstilbene, a One- and Twofold Adiabatic Process

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Abstract: The mechanism of the *Z/E* photoisomerization of a *p*-styrylstilbene has been studied by steady state and time-resolved fluorescence measurements combined with isomerization quantum yield determinations. It was found that on excitation of the *Z,Z* isomer both the isomers, *Z,E* and *E,E*, are produced initially, mainly by adiabatic processes on the singlet excited surface. Quantum mechanical calculations give surface profiles supporting the adopted mechanism.

The mechanism of photoisomerization of stilbenes has been discussed for more than 50 years.² Until a few years ago *Z/E* photoisomerization of olefinic compounds was assumed always to be a diabatic process. In this model the isomerization proceeds via a minimum on the lowest excited singlet or triplet surface where the double bond is twisted 90°. A radiationless transition to the ground-state surface, which has a maximum at this geometry, is followed by a relaxation to either the *Z* or the *E* configuration.

However, in 1983, Tokumaru and co-workers presented strong evidence for an adiabatic *Z/E* isomerization³ on the triplet state surface of a 1-(2-anthryl)-1-butene.⁴ Later, three 9-styryl-anthracenes were shown to isomerize adiabatically on both the excited singlet and triplet state surfaces.⁵

For molecules having a number of double bonds, an adiabatic mechanism allows for more than one isomerization per absorbed photon. Recently, a number of *m*-styrylstilbenes have been studied and the results are stated to be in accordance with a diabatic mechanism.⁶ In contrast, the triplet-sensitized 6-fold *Z/E* isomerization of (*all-Z*)-(2₆)orthoparacyclophene directly to the *all-E* isomer, which we found to occur with a quantum yield of 0.62 in oxygen free benzene, is considered to be an adiabatic process.^{7,8} Extended conjugation seems to be an important factor and we have thus turned our attention first to the photoisomerization of a *p*-styrylstilbene, 1–3. Somewhat surprisingly, its behavior is very different from that of stilbenes and *m*-styrylstilbenes. This *p*-styrylstilbene is, to our knowledge, the first example of a molecule showing twofold adiabatic isomerization on its lowest excited singlet state surface.

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(2) For a review, see: Saltiel, J.; et al. *Org. Photochem.* 1973, 3, 1–113.

(3) In photochemical context the term "adiabatic reaction" refers to a process proceeding on a single electronic state surface, which means that an excited state product is formed.

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