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PHOTOSENSITIZED (ELECTRON TRANSFER) CARBON–CARBON BOND CLEAVAGE OF RADICAL CATIONS

THE DIPHENYLMETHYL SYSTEM†

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Abstract—The photosensitized (electron transfer) reaction of methyl 2,2-diphenylethyl ether (**1**), 1,1,2,2-tetraphenylethane (**5**), 2-methyl-1,1,2-triphenylpropane (**6**), and 2-methoxy-2-diphenylmethylnorbornane (**11** *endo* and *exo*) with 1,4-dicyanobenzene (**4**) in acetonitrile–methanol leads to products indicating cleavage of an intermediate radical cation to give the diphenylmethyl radical and a carbocation. The diphenylmethyl radical is then reduced by the radical anion of the photosensitizer and protonated to yield diphenylmethane. The carbocation fragment reacts with methanol to yield ether and/or acetals. The effect of temperature on the efficiency of cleavage of **5** and **6** has been analyzed. The increase in efficiency observed at higher temperatures reflects an activation energy for the cleavage of the radical cations. In cases where no cleavage is observed, the activation energy for cleavage may be so high that back electron transfer from the radical anion of the photosensitizer is the dominant reaction. The C—C bond dissociation energies of the radical cations of **5** and **6** were estimated by analysis of the thermochemical cycle using the bond dissociation energies and the oxidation potentials of the neutral molecules and the oxidation potential of the diphenylmethyl and cumyl radicals. The direction of cleavage of the radical cation is explained in terms of the relative oxidation potentials of the two possible radicals.

INTRODUCTION

Cleavage of radical cations to the fragments, radical and carbocation, is an important general reaction. This process is well understood in the gas phase where it accounts for many of the fragments in the mass spectrum of a molecule. It is usually possible to predict, or at least explain, not only the site of cleavage, but also the relative probability of the various possible fragmentations.[2] These generalizations are much less well established for the cleavage in solution. Radical cations are common intermediates in solution, easily formed, for example, by photosensitization (electron transfer), and yet reports of C—C bond cleavage are not common. In solution, competing reactions such as loss of a proton, reaction with a nucleophile, or further electron transfer, can be more rapid than C—C bond cleavage.[3] Apparently, both the radical and the carbocation fragments must have considerable stability in order for C—C cleavage to compete with other possible reactions.

Our interest in this area stems from our observation that the radical cation of methyl 2,2-diphenylethyl ether (**1**) generated by electron transfer to 1,4-dicyanobenzene cleaves, yielding diphenylmethane (**2**) and the acetal of formaldehyde (**3**) (Reaction 1).[4] Subsequent studies provided evidence for the mechanism shown in abbreviated form in Scheme 1 (Steps 1–7).

If this process were general, it could have significant synthetic utility.[5] However, our initial attempts to exploit this reactivity showed that the reaction is limited.§ We have therefore initiated a study to determine what factors influence the cleavage process. We hope to answer such questions as: how stable must the two fragments be for cleavage to occur; what factors influence which fragment reacts as the radical and which as the carbocation; is there a stereochemical requirement for cleavage; what is the role of the solvent, for example, in the absence of a nucleophilic solvent could the cleavage process be reversible; and, can the cleavage process be thermally activated?

In this paper we evaluate the generality of C—C bond cleavage using a series of compounds in which the diphenylmethyl radical, or carbocation, is one of the fragments. We chose these compounds because in a preliminary study we found some diphenylmethyl compounds that were readily cleaved whereas some seemingly similar ones were not cleaved at all under these conditions. Furthermore, much is known about the relative stability of the diphenylmethyl radical and carbocation, which will prove useful for the interpretation of the results.

RESULTS

The compounds studied are shown in Chart 1. 1,1,2,2-Tetraphenylethane (**5**),[7] 2-methyl-1,1,2-triphenylpropane (**6**)[8] and 4,4-diphenyl-1-butene (**7**)[9]

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§We have studied the photosensitized (electron transfer) reactivity of 2-methoxy-1-phenylindane and 3-phenyl-2,3-dihydro-4,5-benzofuran. Our hope was that following C—C bond cleavage, the intermediate, which would be a 1,5-radical cation, would cyclize into the terminal phenyl ring and thus afford a convenient synthetic procedure for seven-membered ring compounds. However, no C—C bond cleavage was observed with these compounds.[6]

1 Sensitizer (A) $\longrightarrow$ A*

2 $Ph_2CH{-}R + A^* \longrightarrow Ph_2CH{-}R^{\cdot+} + A^{\cdot-}$

3 $Ph_2CH{-}R^{\cdot+} + A^{\cdot-} \longrightarrow Ph_2CH{-}R + A$

4 $Ph_2CH{-}R^{\cdot+} \longrightarrow Ph_2CH^{\cdot} + R^+$

5 $R^+ + NuH \longrightarrow RNu + H^+$

6 $Ph_2CH^{\cdot} + A^{\cdot+} \longrightarrow Ph_2CH^- + A$

7 $Ph_2CH^- + NuH \longrightarrow Ph_2CH_2 + Nu^-$

4′ $Ph_2CH{-}R^{\cdot+} \longrightarrow Ph_2CH^+ + R^{\cdot}$

5′ $Ph_2CH^+ + NuH \longrightarrow Ph_2CHNu + H^+$

6′ $R^{\cdot} + A^{\cdot-} \longrightarrow R^- + A$

7′ $R^- + NuH \longrightarrow RH + Nu^-$

---

8 $Ph_2CH^{\cdot} + R^+ \rightleftharpoons Ph_2CH^+ + R^{\cdot}$

9 $Ph_2CH^+ + A^{\cdot-} \longrightarrow Ph_2CH^{\cdot} + A$

9 $R^+ + A^{\cdot-} \longrightarrow R^{\cdot} + A$

10 $R^+ \longrightarrow R^{+\prime}$

11 $R^{\cdot} \longrightarrow R^{\prime}$

12 $Ph_2CH{-}R^{\cdot+} \longrightarrow Ph_2\dot{C}{-}R + H^+$

Scheme 1. The mechanism for the photosensitized (electron transfer) C—C bond cleavage.

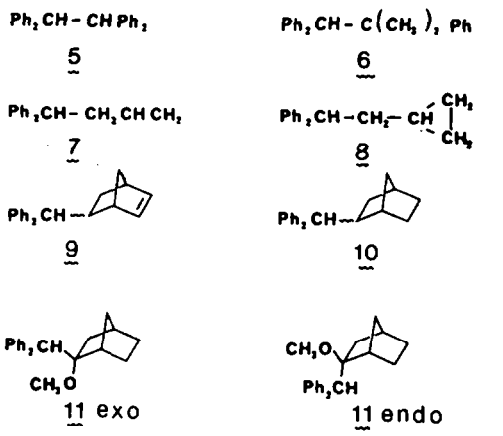


Chart 1. The diphenylmethyl compounds studied.

are known compounds; all other compounds (**8–11**) are new.

The cyclopropyl derivative, 2,2-diphenylethylcyclopropane (**8**), was prepared from the alkene (**7**) by treatment with zinc dust–cuprous chloride and diiodomethane.[10]

The preparation of 5-diphenylmethyl-2-norbornene (**9** *endo* and *exo*) and 2-diphenylmethylnorbornane (**10** *endo* and *exo*) from the known[11] *endo*- and *exo*-methyl-2-norbornene-5-carboxylate is outlined in Scheme 2.

The stereochemistry of the *endo* and *exo* isomers of **9** and **10** was derived from the esters. A thorough analysis of the ^{1}H-NMR spectra of both isomers of **9**, **10** and **13** confirm the structural assignments.

endo-2-Methoxy-*exo*-2-diphenylmethylnorbornane (**11** *exo*) was prepared by the addition of the anion of diphenylmethane to norcamphor, followed by treatment of the alcohol (**14** *exo*) with sodium hydride and then dimethyl sulfate (Scheme 3). The isomer, *exo*-2-methoxy-*endo*-2-diphenylmethylnorbornane (**11** *endo*) was prepared from the exocyclic 2-diphenylmethylenenorbornane (**16**) (Scheme 3). The stereochemical assignments, initially based upon mechanistic considerations, were confirmed by a thorough analysis of the ^{1}H-NMR spectra.

Solutions of **1**, and **5–11** and the photosensitizer 1,4-dicyanobenzene (**4**) in acetonitrile–methanol (3:1) were degassed and then irradiated through a Pyrex filter using a medium-pressure mercury vapour lamp. The irradiation vessel was kept at constant temperature, usually 10° and 80°, by a circulating water bath. Progress of the reaction was followed by gas chromatography (GC) and/or ^{1}H-NMR spectroscopy. The photosensitizer was not consumed.

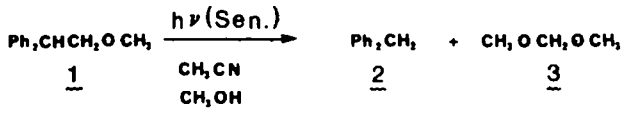
The results of the irradiations, carried out under standard conditions, are reported as percent conversion of the starting material after 18 h (Table 1). Essentially all of the consumed starting material was accounted for by the products listed.

The structural assignments of the known compounds were confirmed by direct comparison (gas chromatography with a mass selective detector (GC/MS), ^{1}H-NMR, and IR spectra) with authentic samples prepared by reported procedures. In the cases of the isomeric methanol adducts (**20**) and the isomeric nitriles (**21**) from **9** (*endo* and *exo*), the structural assignments are incomplete and must be considered tentative. As only trace quantities of the isomers were available, their mixtures were not separated. The structures shown are consistent with the GC/MS analysis and are expected products, based upon the reactivity of other alkenes.†[12a]

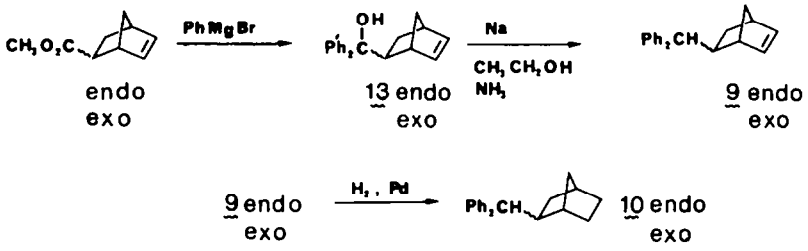
The effect of temperature on the efficiency of the cleavage reactions of 1,1,2,2-tetraphenylethane (**5**) and 2-methyl-1,1,2-triphenylpropane (**6**) was studied in greater detail. Plots of the logarithm of the conversion ($\ln a/(a-x)$) vs time were linear. The results are summarized in Table 2.

†2-Methoxynorbornane and 2-cyanomethylnorbornane are minor products, produced along with the 1:1:1 adducts when 1,4-dicyanobenzene and norbornene are irradiated in acetonitrile–methanol.[12b] The 1:1:1 adducts (**9**:**4**:methanol) are undoubtedly produced in this case as well; but, these products were not isolated.

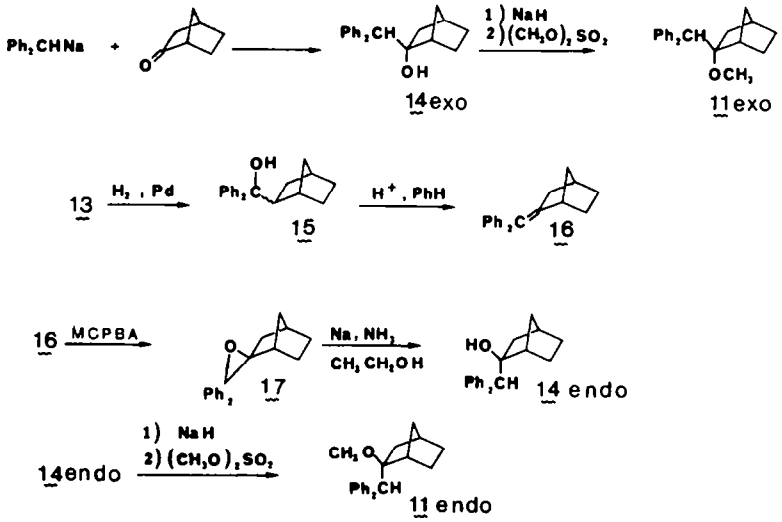
Reaction 1



Sen.= 1,4-Dicyanobenzene (4)



Scheme 2. Preparation of **9** (*endo* and *exo*) and **10** (*endo* and *exo*).



Scheme 3. Preparation of **11** (*endo* and *exo*).

The cyclic voltammograms of **5–11** were characteristic of irreversible electron transfer. The anodic peak positions are listed in Table 3 along with peak potentials of some related compounds measured under identical conditions.

DISCUSSION

The results of the photosensitized (electron transfer) irradiation of **1**, and **5–11** (Table 1) can be described by Steps 1–7 (Scheme 1). Several highly reactive intermediates are obviously involved in this scheme; many other reactions are possible, including those shown in Steps 4′–7′ and 8–12. Nevertheless, this greatly abbreviated sequence can account for all of the results observed thus far.

1,4-Dicyanobenzene (**4**), the electron acceptor, has a long wavelength maximum (290 nm, $\varepsilon = 1600$) extending to 300 nm. The diphenylmethyl chromophores of **1**, and **5–11** have absorption maxima between 245 and 265 nm, which does not extend significantly beyond 270 nm. Irradiation through Pyrex, which absorbs light of wavelengths shorter than 280 nm, is effective in preventing direct irradiation of the donor molecules. The direct irradiation of **5** has been reported;[13] the products thus obtained were not detected upon photosensitization (electron transfer).

The first excited singlet state energy of **4** is 97.6 kcal mol^{-1}, the halfwave reduction potential of **4** is $E^{red}_{1/2} = -1.66$ V (SCE); so, donors with an oxidation potential of $E^{ox}_{1/2} \leq 2.4$ V (SCE) will be oxidized at the diffusion controlled rate.†[3] All com-

†This estimate is based upon the Weller equation[14] assuming the coulombic attraction term is small (1.3 kcal mol^{-1}) in this polar solvent, and that the rate of electron transfer will be diffusion controlled as long as the process is exothermic by at least 5 kcal mol^{-1}.

Table 1. The photosensitized (electron transfer) irradiation of **1**, and **5–11**

Diphenylmethyl compound	Conditions (conversion)	Products, comments
1	[a](*ca* 100)	Diphenylmethane (**2**), formaldehyde dimethylacetal (**3**) (**2**:**3**, 1:1), **5** (trace)[c]
5	[a](0)	No reaction
5	[b](30)	**2**, methyl diphenylmethyl ether (**12**) (**2**:**12**, 1:1)
6	[a](40)	**2**, **5** (trace), 2,3-dimethyl-2,3-diphenylbutane (trace), cumyl methyl ether (**18**) (**2**:**18**, 1:1)[d]
6	[b](65)	**2**, **5** (trace), **18** 2,3-dimethyl-2,3-diphenylbutane (trace) (**2**:**18**, 1:1)[e]
7	[b](0)	[f]
8	[b](0)	[f]
9 *endo*	[b](50)	[f,g]
9 *exo*	[b](60)	[f,g]
10 *endo*	[b](0)	[f]
10 *exo*	[b](0)	[f]
11 *endo*	[a](*ca* 100)	**2**, **5** (trace) 2,2-dimethyloxynorbornane (**22**), norcamphor enol methyl ether (trace), 2,3-dimethoxynorbornane (trace) (**2**:**22**, 1:1)[f]
11 *exo*	[a](*ca* 100)	Results the same as for **11** (*endo*) listed above

[a]Using 1,4-dicyanobenzene (**4**) (0.06 M) as the electron accepting photosensitizer in acetonitrile–methanol (3:1) at 10°. Irradiation through Pyrex for 18 h. Product analysis by NMR.

[b]Conditions the same as in footnote *a* except at 80°.

[c]Ref. 4.

[d]GC/MS indicates about 1% of **12** and cumene (**19**).

[e]Analysis by GC/MS indicates **12** (3%) and **19** (3%) are also produced.

[f]We find no evidence for isomerization or rearrangement of the starting diphenylmethyl compound.

[g]Trace amounts of isomeric ethers (**20**) and nitriles (**21**) were also detected.

pounds studied have oxidation potentials (Table 3) less than this. Therefore, the electron transfer process (Step 2) is favourable in every case. We have previously shown that the fluorescence from 1,4-dicyanobenzene is quenched at nearly the diffusion controlled rate by **1** and by 1,1-diphenylethane.[4]

During the electron transfer step, the electron will be removed from the highest occupied molecular orbital of the donor. Because of the similarity of the oxidation potentials of **1**, and **5–11**, and diphenylmethane and 1,1-diphenylethane (Table 3), it seems likely that the singly occupied molecular orbital (SOMO) will be at least partially associated with the diphenylmethyl moiety. Nevertheless, the variation in oxidation potential that is observed throughout this series is certainly greater than experimental error; and, it is interesting to consider how the rest of the molecule might contribute to the SOMO.

The oxidation potentials of **9** (*endo* and *exo*) are lower than the saturated analogues **10** (*endo* and *exo*). The SOMO of **9** may be associated with the norbornene moiety. The oxidation potential of norbornene ($E^{ox}_{1/2} = 2.02$ V)[15] is essentially the same as that of **9** (*endo* and *exo*); and, the formation of the isomeric ethers (**20**) is a reaction expected of the norbornene radical cation.

The formation of the isomeric nitriles (**21**) may be the result of the addition of the cyanomethyl free radical to the norbornene double bond of **9** (*endo* and *exo*), perhaps involving a chain process.†[12b,16]

The relative reactivities of **1**, and **5–11** can be explained on the basis of a competition between back electron transfer (Step 3) and cleavage of the radical cation (Step 4). In the case of the reactive diphenylmethyl compounds **1**, **5**, **6** and **11** cleavage of the radical cation is fast enough to compete with back electron transfer, whereas for **7–10**, back electron transfer dominates.

In view of the similarity in the oxidation potentials of all these compounds, it seems likely that the rate of the back electron transfer process will also be similar.

†2-Methoxynorbornane and 2-cyanomethylnorbornane are minor products, produced along with the 1:1:1 adducts when 1,4-dicyanobenzene and norbornene are irradiated in acetonitrile–methanol.[12b] The 1:1:1 adducts (**9**:**4**:methanol) are undoubtedly produced in this case as well; but, these products were not isolated.

Table 2. Rate of conversion of the radical cations of **5** and **6** as a function of temperature[a]

Compound	Temperature 25°	40°	50°	60°	70°	80°
5[b]	—	—	1.7×10^{-6}	2.6×10^{-6}	3.1×10^{-6}	4.6×10^{-6}
5[c]	2.5×10^{-5}	4.5×10^{-5}	—	9.4×10^{-5}	—	1.4×10^{-4}
6[b]	9.4×10^{-6}	1.1×10^{-5}	—	1.3×10^{-5}	—	1.5×10^{-5}

[a]These values are not rate constants in the accepted sense. They were obtained from the slope of the line of the plot of the conversion (ln $a/(a-x)$) of the starting material vs time (s) under constant irradiation conditions (see text).
[b]Using 1,4-dicyanobenzene (**4**) as the electron accepting photosensitizer.
[c]Using 1,4-dicyanonaphthalene as the electron accepting photosensitizer.

Table 3. The oxidation potentials of some diphenylmethyl compounds[a]

Diphenylmethyl compound	Ep(V)[b]	$Ep-Ep/2$(mV)
1	2.16[c]	
2 (diphenylmethane)	2.17	120
Diphenylethane	2.16[c]	
5	2.04	110
6	2.00	100
19 (cumene)	2.34	150
7	2.16	120
8	2.09	100
9 *endo*	2.02	100
9 *exo*	2.03	100
10 *endo*	2.16	110
10 *exo*	2.15	110
11 *endo*	1.95	120
11 *exo*	1.95	120

[a]Measured by cyclic voltammetry at a sweep rate of 100 mV s^{-1}, in acetonitrile (0.1 M tetraethylammonium perchlorate).
[b]Peak potential vs SCE. The estimated error is $< \pm 0.02$ V. The oxidation potential ($E^{ox}_{1/2}$) can be taken as 0.03 V less than the anodic peak potential.
[c]Ref. 4. Corrected from $Ag/AgNO_3$ (0.1 M) to SCE by adding 0.34 V.

Accordingly, the variation in reactivity must be the result of variations in the rate of the cleavage process. In the case of the ethers (**1** and **11**), the activation energy for cleavage must be low, so that the reaction is rapid enough to compete with back electron transfer even at 10°. For **7**–**10** the activation energy for cleavage is so high that back electron transfer dominates even at 80°.

The observed temperature dependence of the efficiency of the cleavage of **5** and **6** is particularly revealing. This result implies that the activation energy for cleavage must be in the range where a significant increase in rate can be brought about by increasing the temperature from 10° to 80°.

Table 2 lists the rates of conversion for cleavage of **5** and **6** at several temperatures. Obviously, the magnitude of these individual rates is a complex function which includes rate of formation of excited sensitizer, efficiency of electron transfer, efficiency of deactivation by back electron transfer, etc. A meaningful interpretation of these rates requires more study. However, if these rates are substituted into the Arrhenius equation, the activation energy derived from the slope of the line for the cleavage of **5** with **4** as the electron accepting sensitizer is 7.2 kcal mol^{-1}. When 1,4-dicyanonaphthalene was used as the photosensitizer the activation energy is similar (6.7 kcal mol^{-1}).† The activation energy of the cleavage reaction of **6** with **4** as the photosensitizer is only 1.7 kcal mol^{-1}.

With these estimates for the activation energy for the cleavage of the radical cations of **5** and **6**, it is now possible to estimate the original rate constants. If we assume the preexponential factor has a lower limit of 10^{13}, then an activation energy of 7.2 kcal mol^{-1} would correspond to a rate constant of 10^7–10^8 over the temperature range 10–80°. An activation energy of 1.7 kcal mol^{-1} would correspond to a rate constant of 10^{11}–10^{12} at these temperatures.

It is tempting to associate these numbers with the radical cation cleavage process (Step 4); however, a much more rigorous treatment is required in order to establish the significance of the observed temperature effect. Back electron transfer is also much more complicated than is apparent from the single step depicted in this abbreviated sequence (Step 3).[3b] The rate can depend upon the multiplicity (singlet or triplet) of the geminate radical ion pair. It can depend upon the rate of single–triplet interconversion of this pair and upon the triplet energies of the original donor and acceptor. It can depend upon the rate of diffusional separation of the pair, and upon the exothermicity of the process. In spite of these and other complications there are a few points that can be made.

Since the intersystem crossing of the 1,4-dicyanobenzene singlet is inefficient, and the electron transfer involving this singlet and the donors **1**, and **5**–**11** is rapid, it seems likely that the primary geminate radical ion pair is a singlet.[4] In a number of similar systems the rate constant for separation of the singlet radical ion pair in acetonitrile solution is *ca* 5×10^8 s^{-1}.[17] Competing with separation of the singlet geminate pair is back electron transfer.

There is mounting evidence that the rate of back electron transfer is *inversely* dependent upon the exothermicity of the process, behaviour explained in terms of the gap theory for radiationless decay which

†The singlet of 1,4-dicyanonaphthalene is somewhat less potent as an electron acceptor.[4] Nevertheless, the electron transfer process is still favourable in every case **1**, **5**–**11**. The increased rate of conversion observed with this photosensitizer is the result of greater light absorption. The naphthalene π,π^*-transition extends out beyond 350 nm.

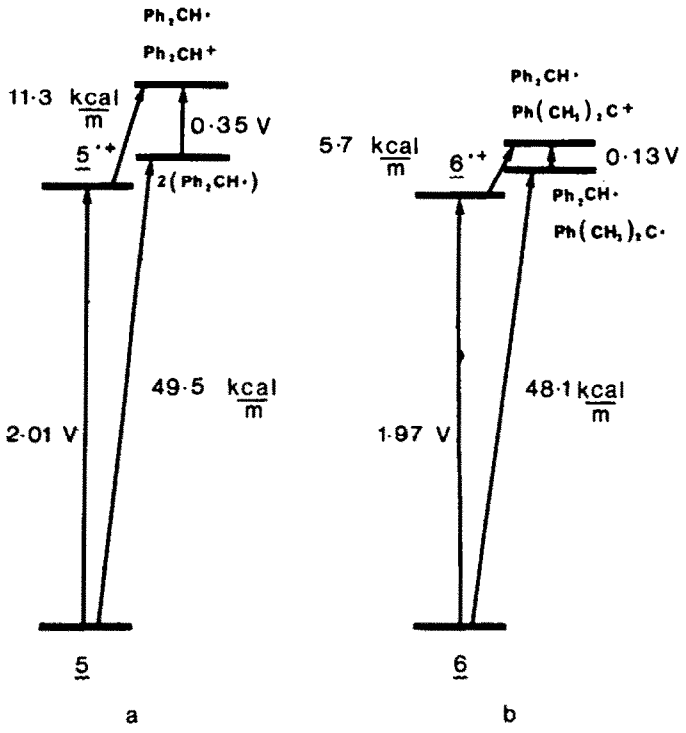


Fig. 1. Thermochemical cycles useful for estimating the bond dissociation energy of the radical cations of: (a) **5**; (b) **6**.

may correspond to the Marcus "inverted region" of electron transfer.[3b,17,18] For example, in two cases similar to those discussed here, the rate constants for back electron transfer were *ca* 2×10^{10} and 10^{9} s^{-1}, respectively, when the exothermicity was 2.1 and 2.8 eV.[3b] Since back electron transfer from the radical anion of **4** to the radical cations of **1**, and **5**–**11** is at least 3.5 eV exothermic, its rate may be considerably slower than solvent separation of the radical ion pair.

The activation energy for radical cation cleavage will reflect the difference in thermodynamic stability between the radical cation and the radical and carbocation fragments; that is, the bond dissociation energy of the radical cation. Of course, this activation energy will also include any activation energy associated with the reverse process, the coupling of the radical and the carbocation. While we are unaware of any experimental data pertinent to this process in solution, there is evidence in the gas phase that for the simple bond cleavage process, the activation energy and the heat of reaction are equal.[19] In solution, there may be an activation energy associated with solvent reorganization; but, in the cases studied here, both the starting radical cation and the product carbocation are highly delocalized and should be solvated to a similar extent and in a similar fashion. If the transition state is also similarly solvated, we believe this factor can be ignored in the first approximation.

We have devised thermochemical cycles and estimated the bond dissociation energy of the central bond in the radical cations of **5** and **6**. For 1,1,2,2-tetraphenylethane (**5**) (Fig. 1(a)), the oxidation potential of the neutral molecule ($E^{ox}_{1/2}$ = 2.01 V) is obtained from the peak potential (Table 3). The oxidation potential of the radical (0.35 V) has been reported.[20] Completing the cycle requires an estimate for the C—C bond dissociation energy in the neutral molecule. This value can be estimated from the heats of formation of **5** and the diphenylmethyl radical calculated using molecular mechanics force field (MM2) calculations.†[21] This type of calculation has been shown to be useful for estimating the bond dissociation energies for similar molecules.[21c] The calculated bond dissociation energy for the central bond of **5** is 49.5 kcal mol^{-1}.

The bond dissociation energy of 1,1,1,2,2-pentaphenylethane has been measured.[22] This value (28.2 kcal mol^{-1}) should be less than the bond dissociation energy of **5** by the additional stabilization and by the additional steric repulsion energy resulting from the fifth phenyl ring.[23] The estimate of 49.5 kcal mol^{-1} for the central bond dissociation energy of **5** seems reasonable. (After this manuscript was submitted, an experimental value (47.5 kcal mol^{-1}) was reported[22b] which is in good agreement.)

Substituting this value into the thermochemical cycle (Fig. 1(a)) gives an estimate for the bond dissociation energy for the central bond in the radical cation of **5** of 11.3 kcal mol^{-1}.

A similar treatment of the data for 2-methyl-1,1,2-triphenylpropane (**6**) is shown in Fig. 1(b). The oxidation potential of the neutral molecule **6** is 1.97 V,

†The calculated heats of formation are: **5** (86.7 kcal mol^{-1}), **6** (53.5 kcal mol^{-1}), diphenylmethyl radical (68.1 kcal mol^{-1}), cumyl radical (33.5 kcal mol^{-1}). These values were obtained using the modified MM2 program.[21]

and the reported[20] oxidation potential of the cumyl radical is 0.13 V. Since the bond dissociation energy for the cleavage of an α-hydrogen or an α-methyl group to give the cumyl and the diphenylmethyl radical indicates the stability of these radicals is very similar[24] and, since **6** will be more sterically hindered than **5**, the central bond in **6** should be somewhat weaker than that in **5**. This reasoning is consistent with the value calculated (48.1 kcal mol^{-1}). Completing the thermochemical cycle (Fig. 1(b)) provides an estimate for the bond dissociation energy in the radical cation of **6** of 5.7 kcal mol^{-1}.

Compounds **1**, and **5–11** have the diphenylmethyl moiety in common, but the remaining fragments offer a significant difference in carbocation or radical stability. The cleavage of the radical cation yielding the diphenylmethyl radical and the various carbocations (Step 4) is favourable as all these fragments lend stability to the carbocation. All fragments would undergo nucleophilic substitution by the unimolecular mechanism (S_N1) if substituted with a good leaving group and in an ionizing medium.

The order of carbocation stabilities is difficult to establish quantitatively. Intuitively, we consider the α-oxycarbocation from **11** the most stable, followed by that formed from **1**, by the cumyl cation from **6**, and the diphenylmethyl cation from **5**. Next would come the allyl cation from **7**: the cyclopropylmethyl cation from **8**, the norbornenyl cation from **9**, and the norbornyl cation from **10**. If the relative rate of the cleavage of the radical cations of **9–11** followed the normal behaviour observed in solvolysis, than the *exo* isomers would react more rapidly than the *endo* isomers.

Compounds **8–11** were chosen specifically, because any reversible cleavage might lead to isomerization and/or rearrangement.[25] If the cyclopropylmethyl cation were formed, then rearrangement products (i.e. allylcarbinyl, cyclobutyl or 2-methylallyl) are to be expected. Similarly, the norbornenyl cation would give the isomerized (*endo–exo*) or rearranged (nortricyclo) derivatives. The norbornyl cations would give rise to geometric and skeletal rearrangement (degenerate in this case).

If the radical cation were to cleave reversibly in the opposite direction, to give the diphenylmethyl cation and the various fragment radicals (Step 4′), rearrangement of the radical is still possible. For example, the cyclopropylmethyl radical rearranges rapidly (1.3×10^8 s^{-1} at 25°) to the 3-butenyl radical.[26]

None of these rearrangements or isomerizations was observed. Apparently, no reversible cleavage of the radical cation **8–10** occurs. In the case of **11**, where relatively efficient cleavage was observed, *no* isomerization, *endo–exo* or *exo–endo*, of recovered starting material was detected. There are several reported examples of isomerization and rearrangement of radical cations;[3b,5b] it seems likely that whether this reaction is observed or not will depend upon the relative rates of the various competing reactions.

On what basis can the products be predicted; which fragment will form the product derived from the radical and which the product from the carbocation? While the answer to this question will require a fundamental understanding of the overall cleavage process, the limited number of examples reported here provides some insight. The results from **6** are particularly useful in this regard.

Consider first the cleavage to the radical and carbocation within the solvent cage. Whether the direction of cleavage is determined initially by the relative rates of Step 4 vs 4′, or whether it is decided by electron transfer within the solvent cage (Step 8), it seems likely that the radical–carbocation distribution within the cage will reflect the difference in the oxidation potentials of the two possible radicals. This ratio should be consistent with the Nernst equation in which case the product ratio will reflect this thermodynamic control

$$E^\circ - E'^\circ = 4.606RT/nF(\log [R'^+]/[R^+]). \quad 13$$

If the difference in the oxidation potentials of the radicals is 0.1 eV, the ratio of the carbocations will be in favour of that with the lower oxidation potential by 7 : 1. If the difference in oxidation potentials is only 0.01 eV, the ratio of carbocations will be 1.2 : 1 at 25°.

From the reported[20] oxidation potentials of the diphenylmethyl radical (0.35 V) and the cumyl radical (0.13 V), the ratio of cumyl to diphenylmethyl cation should be 37 : 1 at 80°. The observed product ratio, 33 : 1, is consistent with this.

If the rate of equilibration of the carbocations (Step 8) continues to be rapid even after the radical and carbocation have diffused apart, then the factor determining the product ratio would be the relative rates of the reactions of the two carbocations with the nucleophile (Step 5 vs 5′). The rate constants for reaction of some carbocations as stable as the diphenylmethyl and cumyl cations, with methanol are known to be relatively small, significantly slower than diffusion; therefore, equilibration is possible.[27] If this kinetic control pertains, there is evidence that the more stable (that is, more highly delocalized) carbocations react slower with methanol than do less stable carbocations.[27]

It is not possible to distinguish between these two possibilities from the limited number of reactive compounds studied here. We have, however, begun a systematic study of how substituents on **5** and **6** affect this product ratio. Preliminary results indicate that the predominant ether is derived from the more stable carbocation.† Therefore, the product ratio is *not* controlled by the relative rates of the reactions of the two carbocations with the nucleophile. Once the radical and the carbocation separate the product ratio is established because the concentration of these intermediates is low, and relatively slow solvent reorganization will influence the rate constant for the equilibration of the radical and carbocation.

The process of cleavage of the radical cation (Step 4) is similar to the fragmentation of the molecular ion in the gas phase. The fundamental difference, and it is certainly not trivial, is that caused by solvation of the radical cation and subsequently the transition

†The photosensitized (electron transfer) cleavage of 1,1-di(4-methylphenyl)-2,2-diphenylethane at 80° gives almost exclusively diphenylmethane, and methyl di(4-methylphenyl)methyl ether in the ratio 1 : 1. Less than 5% of either di(4-methylphenyl)methane or methyl diphenylmethyl ether was detected.[28] Similarly, 2 - (4 - methoxyphenyl) - 2 - methyl - 1,1 - diphenylpropane gives only 4-methoxycumyl methyl ether, while 2 - (4 - trifluoromethylphenyl) - 2 - methyl - 1,1 - diphenylpropane gives equal amounts of both of the ethers.[1]

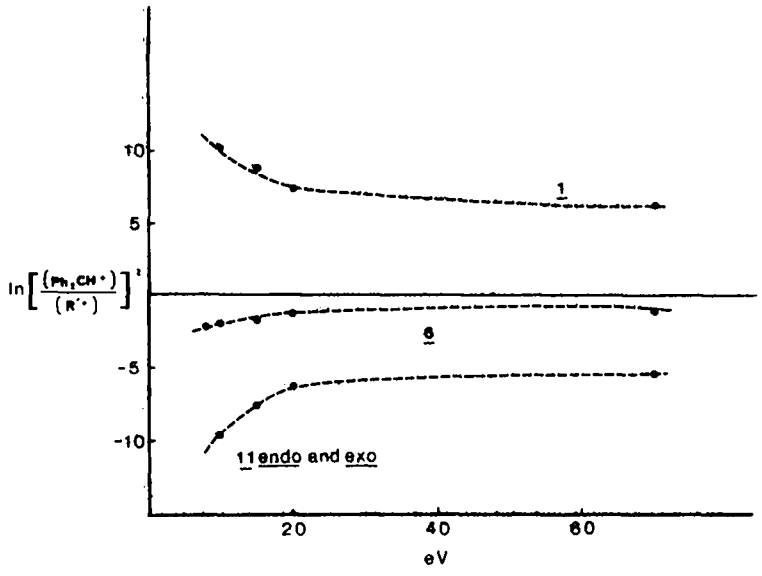


Fig. 2. The effect of ionizing voltage on the fragment ratio Ph_2CH^+/R^+. For 1 (R^+, $m/z = 45$); 6 (119); 11 *endo* and *exo* (125).

state for the cleavage in solution, relative to this process in the gas phase.

We have pointed out that the predominant mode of cleavage of the molecular ion of 1 in the gas phase is to give the diphenylmethyl cation, while no methyl diphenylmethyl ether is observed upon photosensitized cleavage in solution.[4] This difference in behaviour was attributed to the favoured formation of the delocalized ion in the gas phase, while in solution the more localized carbocation was favoured because of polar solvent stabilization.

The effect of variation in the ionizing potential of the mass spectra of 1, 6, and 11 (*endo* and *exo*) on the ratio of the two relevant carbocations is shown in Fig. 2. From these data it is clear that while the α-oxycarbocation is a minor fragment in comparison to the diphenylmethyl cation from 1, in the case of 11 (*endo* and *exo*) the α-oxycarbocation is preferred. The gas phase and solution phase behaviour of the radical cations of 11 (*endo* and *exo*) are more similar than for 1. Of course, the 2-methoxynorbornyl cation is much more stable than the methoxymethyl cation from 1.

In the case of 6, where the energy associated with solvation should be similar for the two possible carbocations, again, both positive fragments are observed in the mass spectrum. In fact, in this case, cleavage to give the cumyl cation is preferred both in the gas phase and in solution.

Another reaction which could compete with C—C bond cleavage of the radical cation is deprotonation (Step 12). We have described thermochemical cycles used to estimate the pK_a of radical cations.[29] We estimate a pK_a of -12.4 for deprotonation of the radical cation of 5 from the diphenylmethyl position.† The pK_a values for the other diphenylmethyl compounds must be similar. Clearly, this process is thermodynamically favourable. The question then is how fast will the deprotonation be?

The limited information available concerning the rate of deprotonation of radical cations such as 1, and 5–11 suggests that this reaction may not be fast enough to compete effectively with rapid back electron transfer. For example, the half-life for proton loss from the toluene radical cation is near 10^{-3} s in acetonitrile,[30] even though its pK_a is -13.[29] Deprotonation of the diphenylmethyl moiety of 1, and 5–11, which has a similar pK_a, could be even slower since the proton is even more hindered to the approach of the base (solvent). Perhaps even more important is the fact that the conformation required for deprotonation, that with the α-C—H bond parallel to the SOMO, is even less favourable.[31]

Some experiments were carried out to determine if these radical cations are deprotonated reversibly. An irradiation was performed initially to demonstrate that Steps 6 and 7 require incorporation of deuterium (d) in the diphenylmethane (2) from 5 in acetonitrile–methanol O-d. At low conversion, one deuterium was incorporated essentially quantitatively in 2. However, at high conversion deuterium was also incorporated, albeit in small amounts, into the benzylic position of 5 and more than one deuterium was incorporated in 2. Furthermore, a control experiment indicated that diphenylmethane incorporates deuterium under these conditions. While these results are consistent with the occurrence of Steps 6 and 7, they also show that the benzylic hydrogens of the diphenylmethyl moiety of 5 and 2 can be exchanged, probably by Step 12.

If this deprotonation reaction were efficient and reversible, it could compete with the cleavage process and might then account for some of the apparent lack of reactivity. However, while some deuterium was incorporated into 5, exchange was inefficient relative to cleavage. Furthermore, little or no deuterium was incorporated into 9 (*endo* or *exo*) or 10 (*endo* or

†Method 1 uses the equation: $pK_a(RH^{+\cdot})_{sol} = (-FE_{RH} + \Delta\theta_{f(H^+)sol} + \Delta G_{BDE(R-H)_g} - \Delta G_{f(H)_g})/2.3RT$.[29]
The $\Delta G_{BDE(R-H)_g}$ used was that for the α-hydrogen of 1,1-diphenylethane (ΔG_{BDE}(1,1-diphenylethane) = 73 kcal mol^{-1}).[24a]

exo) under these conditions. Apparently, the rate of deprotonation from these radical cations is slow relative to back electron transfer.

CONCLUSIONS

Several questions concerning the fragmentation of radical ions have been answered, at least qualitatively. Cleavage occurs only if the fragment radical and carbocation have stabilities comparable to the diphenylmethyl intermediates. The product ratio reflects the difference in oxidation potential of the two possible radicals: the fragment radical with the lower oxidation potential will react as the carbocation. Cleavage of the radical cation is not generally reversible. The cleavage process can be thermally activated, and it seems likely that the thermal barrier reflects the bond dissociation energy of the radical cation. While the reaction has limitations it will have considerable synthetic utility, particularly in cyclic systems where 1,*n*-radical ions are involved. This reaction may also find use as a method to remove photolabile protecting groups for aldehydes, ketones or alcohols.

EXPERIMENTAL

General methods. ^{1}H- and ^{13}C-NMR spectra were recorded on a Varian CFT-20 or a Nicolet NB NMR spectrometer and are reported in ppm downfield from TMS. IR spectra were recorded on an air-purged Perkin–Elmer 180 grating IR spectrometer and are reported in wavenumbers (relative to the 1601.8 cm^{-1} absorption of polystyrene). UV–vis absorption spectra were recorded on a Cary–Varian 219 absorption spectrometer and are reported in nanometers. MS were recorded on a modified Du Pont CEC model 21–104 mass spectrometer at 70 eV (unless otherwise noted) or a Hewlett–Packard 5970 series mass selective detector (HP) and are reported as *m/z* (relative intensity). Elemental analyses were performed by Canadian Microanalytics Services Inc. (Vancouver, Canada) or Guelph Chemical Laboratories Ltd. (Guelph, Ontario) and agreed to within 0.3% of the calculated values. The m.ps were determined using a Cybron Corporation Thermolyne m.p. apparatus and are corrected. The MM2 calculations were carried out on a Perkin–Elmer 3230 computer.

Product analyses were determined by vapour phase chromatography using either a Hewlett–Packard 5990 GC (25 m methyl silicone fused silica capillary column (0.20 mm i.d.)) coupled to a HP 5970 mass selective detector; or, a Varian Aerograph 1200 (1/8 in × 6 ft Cu columns packed with 10 or 20% SE-30 on Chromosorb W 60/80 NAW unless otherwise noted). All liquid compounds were purified by preparative vapour phase liquid chromatography using an Aerograph Autoprep A-700 (3.8 in × 6 ft aluminium columns packed with 5 or 10% SE-30 on Chromosorb 60/80 NAW). Preparative medium pressure liquid chromatography[12a] (MPLC) was carried out using a 25 × 1000 mm column packed with TLC grade silica gel (without binder) (Merck) at 15 psi (helium) with hexanes. The columns were eluted with a hexanes/methylene chloride gradient and the eluent was monitored/collected by a UV spectrometer/fraction collector.

Materials. Acetonitrile (Fisher ACS grade) was distilled successively from NaH and P_2O_5, passed through a column of basic alumina; it was then refluxed over CaH_2 for 24 h (N_2 atmos) and fractionally distilled before use. All solvents were fractionally distilled. 1,4-Dicyanobenzene (Aldrich) was purified by first stirring with Norite in CH_2Cl_2 and then was sublimed and recrystallized from 95% EtOH. 1,4-Dicyanonaphthalene was prepared by the method of Heiss *et al.*[32] and purified by vacuum sublimation, column chromatography (neutral alumina, Merck) and was then recrystallized three times from MeOH. Tetraethylammonium perchlorate (Aldrich) was recrystallized (3 times) from 95% EtOH and dried in a vacuum oven (12 h at 80°, 10 Torr) before use.

Photosensitized (electron transfer) irradiations were carried out in acetonitrile–MeOH (3:1) at a substrate concentration of 0.1 M and photosensitizer concentration of 0.02 M. Solns were placed in 2 cm i.d. Pyrex tubes or 5 mm Pyrex NMR tubes, flushed with dry N_2 and sealed. A Hanovia 450 W medium pressure mercury vapour lamp with a quartz cooling jacket was used for all irradiations. The irradiation tubes were placed in a Pyrex vessel, which has a built in cooling jacket which also served as a short wavelength (< 280 nm) filter, connected to a Julabo Model F10V circulating water bath. Reaction mixtures were chromatographed by MPLC. For quantitative studies, changes of the ratio between starting material and products were followed by ^{1}H-NMR.

Cyclic voltammetric measurements. Oxidation potentials were obtained by cyclic voltammetry using an apparatus which is similar to that previously described.[33] The working electrode was a Pt sphere (1 mm diam), while the counter electrode was a Pt wire. The reference electrode was a saturated calomel electrode (SCE) which was connected to the soln by a Luggin capillary. The electrolyte used was 0.1 M tetraethylammonium perchlorate in acetonitrile. Substrate concentrations were typically 0.005 M. If the electron transfer process was not reversible, the half-wave potential was taken as 0.028 V before the anodic peak potential.[34]

Preparation of diphenylmethyl compounds

1,1,2,2-Tetraphenylethane (**5**). Chlorodiphenylmethane was prepared from benzhydrol (9.2 g, 0.05 mol) using $SOCl_2$ (9.0 g, 0.075 mol) in CCl_4 (100 ml). The solvent and volatile products were evaporated and the residue dissolved in ether (100 ml) and Na (3.7 g, 0.16 at. eq.) was added in small pieces to the soln. The mixture was refluxed for 2 days. The soln was extracted with CH_2Cl_2, dried over $MgSO_4$ and evaporated. The resulting 1,1,2,2-tetraphenylethane was recrystallized from benzene–EtOH to give 3.8 g (45%) pure product (m.p. 208–209°; lit.[7] 213°). ^{1}H-NMR (361.1 MHz, $CDCl_3$) δ: 7.4–6.9 (m, 20H), 4.77 (s, 2H). ^{13}C-NMR (20 MHz, $CDCl_3$) δ: 143.4, 131–126 (m), 124.8, 57–55 (m). IR (KBr) cm^{-1}: 3040, 2910, 1610, 1500, 1460, 1080, 1040, 750, 700, 610, 565. MS (Du Pont): 334 (M^+, 1.5), 168 (15), 167 (100), 166 (6), 165 (15), 152 (9), 115 (2).

Cumyl diphenylmethane (**6**). Cumyl chloride, prepared by the method of Olah *et al.*,[35] was used without further purification. Diphenylmethane (6.7 ml, 0.04 mol) in anhyd diethyl ether (10 ml) was added dropwise over 30 min to a stirred soln of sodium amide (1.6 g, 0.04 mol) in liquid ammonia (50 ml). The mixture was stirred for 1 h, and the chloride was added dropwise over 30 min. The reaction was stirred for 1 h, the ammonia was then allowed to evaporate and the mixture was washed with sat NH_4Cl aq and water. The soln was dried over $MgSO_4$ and the solvent was evaporated. The product was purified by MPLC and recrystallized from 95% EtOH. The yield of **6** was 6.8 g (59%) (m.p. 68.5–69.5°). ^{1}H-NMR (361.1 MHz, $CDCl_3$) δ: 7.4–6.9 (m, 15H), 4.16 (s, 1H), 1.42 (s, 6H). ^{13}C-NMR (20 MHz, $CDCl_3$) δ: 142.1, 132–124 (m), 64 (d), 42.0, 28 (q). IR (KBr) cm^{-1}: 2980, 1610, 1505, 1460, 1100, 1045, 780, 715, 700, 600. MS (Du Pont): 167 (51), 165 (13), 152 (6), 119 (100), 118 (5), 115 (3), 91 (20). Electrochemistry: $E^{ox}_{1/2}$ = 2.00 V vs SCE.

4,4-Diphenyl-1-butene (**7**). Compound **7** was prepared by the method of Kuznetsov *et al.*[36] The product was purified by vacuum distillation (87°, 0.2 Torr). The yield of **7** was 24.7 g (66%). ^{1}H-NMR (361.1 MHz, $CDCl_3$) δ: 7.3–7.1 (m, 10H), 5.8–5.6 (m, 1H), 5.02 (dd, 1H), 4.93 (dd, 1H), 4.0 (t, 1H), 2.8 (t, 2H). ^{13}C-NMR (20 MHz, $CDCl_3$) δ: 144.4, 129–127 (m), 125.0, 120.0, 92.1, 51 (d), 40 (t). IR (KBr) cm^{-1}: 3040, 1650, 1610, 1500, 1460, 915, 740, 700.

2,2-Diphenylcyclopropylethane (**8**). 4,4-Diphenylbutene was converted to **8** by the procedure of Rawson and Harri-

son.[10] The crude product was purified by vacuum distillation to give **8** (7.8 g, 77% yield). ^{1}H-NMR (361.1 MHz, $CDCl_3$) δ: 7.3–7.1 (m, 10H), 4.0 (t, 1H), 1.9 (t, 2H), 0.6 (m, 1H), 0.4 (m, 1H), 0.1 (m, 2H). ^{13}C-NMR (20 MHz, $CDCl_3$) δ: 145.1, 128.2, 127.8, 125.8, 51.5, 40.8, 9.6, 4.7. IR (KBr) cm^{-1}: 3040, 2930, 1610, 1500, 1460, 1025, 750, 700. MS (HP): 222 (M^+, 29), 168 (100), 167 (61), 166 (64), 115 (52), 104 (89), 91 (34), 77 (34), 55 (42), 51 (45), 39 (78), 29 (68), 27 (68).

Methyl norbornene-5-carboxylate (*endo and exo*). This was prepared by the addition of methyl acrylate to a soln of cyclopentadiene in EtOAc.[11] The crude product after isolation was found to be a mixture of approximately 70% *endo* and 30% *exo* which was separated by GC using 1/8 in × 6 ft 20% Carbowax 20M on Chromosorb W 60/80 at 90°.

endo-5-*Diphenylhydroxymethylnorbornene* **13** (*endo*). Ester (15.22 g, 0.1 mol) (a mixture of the *endo* and *exo* isomers, dissolved in anhyd diethyl ether) was added dropwise to 0.3 mol of PhMgBr at 0°. The mixture was allowed to stir for 24 h at room temp. The reaction was quenched by an iced soln of NH_4Cl which was then extracted with diethyl ether. The combined organic layers were washed twice with sat NaCl aq, dried with $MgSO_4$ and the solvent was evaporated. The residue, oil and crystals, was dissolved in the minimum quantity of hot EtOH and the crystals (14.02 g, 51% obtained upon cooling were recrystallized once again. The yield of pure **13** (*endo*) was 9.43 g (34%) obtained as colourless needles (m.p. 107–107.5°). ^{1}H-NMR (361.1 MHz, $CDCl_3$) δ: 7.50–7.10 (m, 10H; aromatic), 6.32 (dd, 1H; H_2, $^3J(H_2, H_3) = 5.7$ Hz, $^3J(H_2, H_1) = 3.2$ Hz), 6.13 (dd, 1H; H_3, $^3J(H_3, H_4) = 2.9$ Hz), 3.39 (ddd, 1H; H_{5exo}, $^3J(H_{5exo}, H_4) = 3.1$ Hz, $^3J(H_{5exo}, H_{6exo}) = 8.2$ Hz, $^3J(H_{5exo}, H_{6endo}) = 5.2$ Hz), 2.84 (brs, 1H; H_1), 2.58 (brs, 1H; H_4), 2.50 (s, 1H; OH), 1.96 (brd, 1H; H_{7a}, $^2J(H_{7a}, H_{7s}) = 8.1$ Hz), 1.93 (ddd, 1H; H_{6exo}, $^2J(H_{6exo}, H_{6endo}) = 12.0$ Hz, $^3J(H_{6exo}, H_1) = 4.0$ Hz), 1.37 (brs, 1H; H_{7s}), 1.14 (ddd, 1H; H_{6endo}, $^4J(H_{6endo}, H_{7s}) = 2.8$ Hz). ^{13}C-NMR (90 MHz, $CDCl_3$) δ: 148.99, 148.06, 139.14, 132.69, 127.94, 126.91, 126.13, 125.87, 125.52, 78.96, 51.22, 48.25, 45.00, 43.00, 29.33. IR (KBr): 3535 (s), 3050 (m),2960 (s), 2935 (s), 2885 (m), 1490 (s), 1440 (s), 1160 (b), 980 (m), 740 (s), 690 (s). UV (hexanes): $\lambda_{max} = 257$ nm ($\varepsilon = 401$). MS (Du Pont): 276 (17), 183 (92), 105 (100), 66 (17).

exo-*Methyl norbornene-5-carboxylate*. The mixture of esters (20.0 g, 0.13 mol) (70% *endo* and 30% *exo*) was equilibrated with a soln of 300 ml of MeOH–NaOMe. GC analysis of the product (1/8 in × 6 ft 20% Carbowax 20M on Chromosorb W 60/80 at 90°) indicated a composition of 53% *exo* and 47% *endo*. A 2 g portion of this mixture was purified using MPLC eluting with hexanes. The first compound to elute was the *exo* ester (**12** *exo*) (720 mg as a colourless liquid) overlapping slightly with the *endo* ester (**12** *endo*) (890 mg as a colourless liquid).

exo-*Ester*. ^{1}H-NMR (361.1 MHz, $CDCl_3$) δ: 6.15–6.09 (m, 2H; vinyl), 3.69 (s, 3H; OCH_3), 3.04 (brs, 1H; bridgehead), 2.92 (brs, 1H; bridgehead), 2.26–2.21 (m, 1H), 1.95–1.89 (m, 1H), 1.54–1.52 (d, 1H), 1.43–1.34 (m, 2H). ^{13}C-NMR (90 MHz, $CDCl_3$) δ: 176.70, 138.02, 135.70, 51.70, 46.57, 46.37, 42.99, 41.63, 30.35.[36]

endo-*Ester*. ^{1}H-NMR (361.1 MHz, $CDCl_3$) δ: 6.19–6.17 (dd, 1H), 5.94–5.91 (dd, 1H), 3.61 (s, 3H), 3.20 (s, 1H), 2.97–2.92 (m, 1H), 2.90 (s, 1H), 1.94–1.87 (m, 1H), 1.44–1.40 (m, 1H), 1.27 (d, 1H), 0.90–0.85 (m, 1H). ^{13}C-NMR (90 MHz, $CDCl_3$) δ: 175.17, 137.68, 132.32, 51.43, 49.60, 45.64, 43.16, 42.51, 29.25.[36]

exo-5-(*Diphenylhydroxymethyl*)-*norbornene* **13**. The reaction was repeated as described above for the *endo* alcohol (**13**) but pure *exo* ester (1.168 g, 7.7 mmol) was used. The yield of **13** (*exo*), obtained as a viscous yellow oil, was 2.15 g. This oil was chromatographed on a 45 × 400 mm column packed with silica gel and eluting first with hexanes. When all the biphenyl had eluted, the eluent was changed to CH_2Cl_2. Alcohol **13** (*exo*) was recovered as a viscous colourless oil which was further purified by Kugelrohr distillation. ^{1}H-NMR (361.1 MHz, C_6H_6) δ: 7.50–6.80 (m, 10H; aromatic), 6.09 (dd, 1H; H_3, $^3J(H_3, H_2) = 5.6$ Hz, $^3J(H_3, H_4) = 2.6$ Hz), 5.96 (dd, 1H; H_2, $^3J(H_2, H_1) = 2.3$ Hz), 2.59 (brs, 1H; H_1, $^3J(H_1, H_{6exo}) = 3.7$ Hz), 2.48 (brs, 1H; H_4) 2.41 (brdd, 1H; H_{5endo}, $^3J(H_{5endo}, H_{6endo}) = 8.2$ Hz, $^3J(H_{5endo}, H_{6exo} = 4.7$ Hz), 1.58 (brd, 1H; H_{7s}, $^2J(H_{7a}, H_{7s}) = 8.0$ Hz), 1.48 (s, 1H; OH), 1.31 (ddd, 1H; H_{6exo}, $^2J(H_{6endo}, H_{6exo}) = 11.4$ Hz), 1.21 (brd, 1H; H_{7a}, $^4J(H_{7a}, H_{6endo}) = 2.4$ Hz), 1.00 (ddd, 1H; H_{6endo}). ^{13}C-NMR (20 MHz, $CDCl_3$) δ: 147.7, 147.6, 138.3, 137.2, 128.0, 127.8, 126.4, 126.2, 126.0, 125.8, 125.7, 125.5, 79.4, 47.9, 46.3, 43.6, 41.5, 28.3. IR (neat): 3575 (br), 3160 (m), 2970 (s), 2870 (w), 1600 (w), 1490 (m), 1445 (s), 1330 (m), 1070 (m), 970 (m), 730 (s), 690 (s). UV (hexanes): $\lambda_{max} = 257$ nm ($\varepsilon = 608$). MS (HP): M^+ 276 (5), 183 (85), 105 (100), 77 (41).

endo-5-*Diphenylmethylnorbornene* **9**. This reaction was performed in an insulated 250 ml round bottom flask equipped with a dry-ice condenser, $CaCl_2$ drying tube and a gas inlet tube. Into the flask was condensed 120 ml of anhyd ammonia. *Endo* **13** (4.0 g, 15 mmol) was dissolved in 1.47 g (32 mmol) of anhyd EtOH and 50 ml anhyd diethyl ether and added to the ammonia in portions. Na metal (0.74 g, 32 mmol) was added to the mixture over a period of 45 min. After stirring for 1.5 h, the ammonia was allowed to evaporate and 50 ml of diethyl ether, 50 ml of water, and a small amount of ammonium chloride were added to dissolve the basic salts. The aqueous layer was extracted three times with diethyl ether. The combined organic extracts were washed with NaCl aq, dried over $MgSO_4$ and evaporated. The crude yield was 3.6 g obtained as a colourless waxy solid. A 1.5 g portion of this mixture was purified by MPLC (eluting with hexanes). The first compound to elute was 127 mg (8%) of *endo* **10** followed by 1026 mg (63%) of *endo* **9**. Then **10** (*endo*) was recrystallized from 95% EtOH as colourless crystals (m.p. 67°); **9** (*endo*) was also recrystallized from EtOH to give colourless crystals (m.p. 67–68°).

endo-5-*Diphenylmethylnorbornene* **9**. ^{1}H-NMR (361.1 MHz, $CDCl_3$) δ: 7.29–7.09 (m, 10H; aromatic), 6.22–6.19 (dd, 1H; H_2, $^3J(H_2, H_1) = 2.8$ Hz, $^3J(H_2, H_3) = 5.7$ Hz), 6.03–6.00 (dd, 1H; H_3, $^3J(H_3, H_4) = 2.3$ Hz), 3.28 (d, 1H; H_a, $^3J(H_a, H_{5exo}) = 12.0$ Hz), 2.96–2.89 (dddd, 1H; H_{5exo}, $^3J(H_{5exo}, H_4) = 4.3$ Hz, $^3J(H_{5exo}, H_{6exo}) = 8.1$ Hz, $^3J(H_{5exo}, H_{6endo}) = 4.5$ Hz), 2.78 (brs, 1H; H_1, $^3J(H_1, H_{6exo}) = 3.9$ Hz), 2.54 (brs, 1H; H_4), 1.87–1.80 (ddd, 1H; H_{6exo}, $^2J(H_{6exo}, H_{6endo} = 11.8$ Hz), 1.42–1.38 (m, 1H; H_{7a}, $^2J(H_{7a}, H_{7s}) = 8.1$ Hz, $^4J(H_{7a}, H_{6endo}) = 2.7$ Hz), 1.30 (d, 1H; H_{7s}), 0.60–0.45 (dddd, 1H; H_{6endo}). ^{13}C-NMR (20 MHz, $CDCl_3$) δ: 137.5, 132.4, 128.3, 127.6, 125.8, 56.6, 49.3, 44.8, 43.9, 42.8, 31.9. IR (KBr): 3020 (m), 2955 (s), 2947 (s), 2860 (m), 1590 (m), 1490 (s), 1440 (s), 1330 (m), 1070 (m), 1030 (m), 740 (s), 725 (m), 693 (s). UV (hexanes): $\lambda_{max} = 258$ nm ($\varepsilon = 507$). MS (HP): M^+ 260 (50), 194 (82), 193 (100), 165 (76), 115 (93). (Found: C, 92.22; H, 7.92. Calc: C, 92.26; H, 7.74%.)

endo-2-*Diphenylmethylnorbornane* **10**. ^{1}H-NMR (361.1 MHz, $CDCl_3$) δ: 7.34–7.10 (m, 10H; aromatic), 3.71 (d, 1H; H_a, $^3J(H_a, H_{2exo}) = 12.1$ Hz), 2.76–2.69 (m, 1H; H_{2exo}), 2.18 (brs, 1H), 1.99 (brs, 1H), 1.74–1.64 (m, 2H), 1.56–1.41 (m, 1H), 1.35 (d, 1H), 1.30–1.18 (m, 3H), 0.69–0.64 (m, 1H). ^{13}C-NMR (20 MHz, $CDCl_3$) δ: 128.2, 128.0, 127.7, 126.0, 125.8, 68.0, 39.7, 39.0, 36.3, 30.2, 22.6. IR (KBr): 3020 (m), 2950 (s), 2860 (m), 1490 (m), 1447 (m), 740 (s), 700 (vs). UV (hexanes): $\lambda_{max} = 259$ nm ($\varepsilon = 351$). MS (HP): M^+ 262 (40), 167 (100), 165 (53), 95 (42), 67 (38). Electrochemistry: $E^{ox}_{1/2} = 2.13$ V vs SCE. (Found: C, 91.82; H, 8.31. Calc: C, 91.55; H, 8.45%.)

exo-5-*Diphenylmethylnorbornene* **9**. The reaction was repeated as described above for the *endo* isomer with 500 mg (18 mmol) of the *exo* alcohol **13**. The crude yield of **9** (*exo*) was 413 mg (88%). This was purified by MPLC and 229 mg (49%) of *exo* **9** was recovered. *Exo* **10** was not detected by ^{1}H-NMR and GC. The product was recrystallized from ethanol to give colourless crystals of **9** (*exo*), m.p. 53.5–54.5°. ^{1}H-NMR (361.1 MHz, $CDCl_3$) δ: 7.29–7.12 (m, 10H; aromatic), 6.04 (s, 2H; H_2, H_3), 3.59 (d, 1H; H_a, $^3J(H_a, H_{5endo}) = 12.0$ Hz), 2.77 (brs, 1H; H_1), 2.39 (brs, 1H; H_4),

2.28–2.20 (m, 1H; H_{5endo}), 1.51 (d, 1H; H_{7s}, $^3J(H_{7s}, H_{7a}) = 8$ Hz), 1.31 (d, 1H; H_{7a}), 1.26–1.20 (dd, 1H; H_{6endo}, $^3J(H_{6endo}, H_{6exo}) = 12$ Hz, $^3J(H_{6endo}, H_{5endo}) = 8.6$ Hz), 1.14–1.09 (m, 1H; H_{6exo}, $^3J(H_{6exo}, H_{5endo}) = 4.8$ Hz). ^{13}C-NMR (90 MHz, $CDCl_3$) δ: 136.94, 136.90, 128.41, 128.28, 128.07, 127.89, 125.94, 58.02, 45.12, 44.60, 43.46, 42.28, 32.93. IR (melt): 3060 (m), 3030 (m), 2970 (s), 2870 (w), 1600 (m), 1490 (s), 1450 (s), 1330 (s), 1030 (w), 895 (w), 735 (s), 695 (s). MS (HP): M^+ 260 (45), 194 (100), 181 (87), 180 (86), 179 (82), 167 (70), 116 (84), 66 (94). UV (hexanes): $\lambda = 258$ nm ($\varepsilon = 386$).

exo-2-*Diphenylmethylnorborane* **10**. Compound **10** (*exo*) was prepared by the catalytic hydrogenation of *exo* **9** (452 mg, 1.7 mmol). To 50 ml of dry diethyl ether in a 100 ml 3-necked flask was added 100 mg of 5% Pd on C and the flask was charged with H_2 at 900 mm Hg. The soln was stirred for 18 h at room temp, filtered through a bed of Celite and the solvent was evaporated. The yield of **10** (*exo*) obtained as a colourless solid was 0.374 g (82%), m.p. 43–44°. ^{1}H-NMR (361.1 MHz, $CDCl_3$) δ: 7.38–7.08 (m, 10H; aromatic), 3.48 (d, 1H; H_a, $^3J(H_a, H_{2endo}) = 12.0$ Hz), 2.33–2.19 (m, 1H; H_{2endo}, $^3J(H_{2endo}, H_{3exo}) = 4.9$ Hz), 2.50–2.43 (brs, 1H; H_1), 1.91 (brs, 1H; H_4), 1.55–1.45 (m, 3H), 1.34–1.28 (m, 1H; H_{3exo}), 1.22–1.12 (m, 2H), 1.09–1.00 (m, 2H). ^{13}C-NMR (20 MHz, $CDCl_3$) δ: 145.6, 144.0, 128.4, 128.2, 128.1, 127.9, 125.8, 118.2, 57.6, 39.3, 37.6, 37.0, 35.2, 30.2, 28.7. IR (melt): 3090 (w), 3070 (w), 3030 (m), 2950 (s), 2910 (m), 2880 (m), 1600 (w), 1495 (s), 1450 (s), 1320 (w), 1305 (w), 1070 (w), 1030 (w), 740 (s), 695 (s). UV (hexanes): $\lambda_{max} = 260$ nm ($\varepsilon = 485$). MS (HP): M^+ 262 (19), 167 (99), 95 (100). (Found: C, 91.45; H, 8.64. Calc: C, 91.55; H, 8.45%.)

exo-2-(*Diphenylmethyl*)-2-*hydroxynorbornane* **14**. Into a 150 ml 3-necked flask was condensed 60 ml of anhyd ammonia. A catalytic amount of anhyd $FeCl_3$ was added followed by 0.05 g of Na metal. The resulting blue colour was discharged by bubbling air through the mixture until the soln turned black (*ca* 5 min). The remaining Na (1.0 g, 45 mmol) was then added in small pieces over a period of 10 min and the mixture was allowed to stir for 1.5 h. Then 5.0 g (30 mmol) diphenylmethane in 20 ml anhyd diethyl ether was added slowly. The resulting orange soln was allowed to stir for 0.5 h and 3.47 g (30 mmol) of norcamphor, dissolved in 50 ml of anhyd diethyl ether was added dropwise to the reaction. When the addition was complete the resulting soln was allowed to warm to room temp. The excess sodium amide was quenched with MeOH and the soln was poured into iced HCl aq. The mixture was extracted with diethyl ether and the combined organic layers were washed with sat $NaHCO_3$ aq, sat NaCl aq, dried with $MgSO_4$ and the solvent was evaporated. The resulting oil was purified by chromatography using a 45 × 400 mm silica gel column, eluted with a hexanes–CH_2Cl_2 gradient. Diphenylmethane (1.81 g) and tetraphenylethane (209 mg) were the first compounds to elute, followed by **14** (*exo*; 1.5 g). This crude product was recrystallized from alcohol. The yield of pure **14** (*exo*; m.p. 108.5–109°) was 30% based on recovered starting materials. ^{1}H-NMR (361.1 MHz, $CDCl_3$) δ: 7.57–7.14 (m, 10H; aromatic), 4.01 (s, 1H; H_a), 2.24 (brs, 1H), 2.17 (brs, 1H), 1.87–1.80 (m, 1H), 1.72–1.65 (m, 2H), 1.60 (s, H; OH), 1.58–1.48 (m, 1H), 1.34–1.17 (m, 4H). ^{13}C-NMR (20 MHz, $CDCl_3$) δ: 141.7, 141.6, 129.8, 129.2, 128.0, 127.8, 126.1, 125.4, 81.2, 60.1, 45.6, 45.5, 38.4, 37.0, 28.0, 22.0. MS (HP): M^+ 278 (1), 168 (100), 167 (41), 111 (72).

exo-2-(*Diphenylmehyl*)-2-*methoxynorbornane* **11**. The pure alcohol **14** (*exo*) (1.21 g 4.4 mmol) dissolved in 30 ml of anhyd diethyl ether, was added via a constant pressure dropping funnel, to a 100 ml 3-necked flask containing 30 ml anhyd diethyl ether and 1.0 g (40 mmol) NaH (50% oil dispersion washed three times with pentane). After the initial reaction had subsided, 5.0 g (40 mmol) Me_2SO_4 was added to the stirred soln. The mixture was refluxed for 18 h and was then poured into NH_4Cl aq. The aqueous soln was extracted with ether (3 times) and the combined organic layers were washed successively with sat NaCl aq, conc NH_4OH (to destroy excess Me_2SO_4), sat NaCl aq, and was then dried with $MgSO_4$. The crude product (1.44 g) was chromatographed using silica gel (hexanes–CH_2Cl_2 gradient). Pure **11** (*exo*; 720 mg) was obtained as a colourless solid (m.p. 52–53°) along with 400 mg of less pure product. ^{1}H-NMR (361.1 MHz, $CDCl_3$) δ: 7.42–7.15 (m, 10H; aromatic), 4.35 (s, 1H; H_a), 3.07 (s, 3H; OCH_3), 2.55 (brs, 1H), 2.14–2.06 (m, 2H), 1.82–1.78 (m, 1H), 1.55–1.47 (m, 2H), 1.36–1.28 (m, 2H), 1.02–0.99 (brd, 1H), 0.75–0.72 (brd, 1H). ^{13}C-NMR (20 MHz, $CDCl_3$) δ: 142.8, 142.4, 130.4, 130.0, 129.8, 127.9, 126.1, 125.7, 87.1, 58.2, 52.8, 45.4, 41.3, 38.0, 36.5, 28.5, 23.5. IR (melt) cm^{-1}: 3060 (w), 3030 (w), 2950 (s), 2830 (m), 1600 (w), 1495 (s), 1450 (s), 1110 (m), 1080 (s), 970 (w), 740 (m), 695 (s). UV (hexanes): $\lambda_{max} = 259$ nm ($\varepsilon = 569$). MS (HP): M^+ 292 (0.3), 165 (15), 125 (100), 93 (50). (Found: C, 86.21; H, 8.21. Calc: C, 86.25; H, 8.27%.)

2-*Diphenylmethylenenorbornane* **16**.[38] The norbornene alcohols **13** (*endo* and *exo*) (1.0 g 3.6 mmol) in 30 ml of anhyd diethyl ether were reduced by catalytic hydrogenation (25°, 900 mm Hg) using 100 mg 5% Pd on C and 100 mg of K_2CO_3. The mixture (after 18 h) was filtered through Celite and the solvent was evaporated. The reduction was complete as determined by GC. The crude alcohols were then dehydrated by refluxing with 100 mg *p*-toluenesulfonic acid in 30 ml benzene for 3/4 h. The mixture was cooled, K_2CO_3 was added, the soln filtered and the solvent evaporated. Pure **16** was obtained by recrystallization from MeOH as lustrous plates (m.p. 68–69°). ^{13}C-NMR (20 MHz, $CDCl_3$) δ: 145.7, 147.9, 129.2, 127.9, 127.7, 125.8, 42.9, 39.6, 39.2, 36.5, 29.6, 28.2. IR (KBr): 3060 (m), 2962 (s), 2872 (m), 1640 (w), 1600 (m), 1495 (s), 1440 (s), 760 (s), 695 (s). UV (hexanes): $\lambda = 250$ nm ($\varepsilon = 12{,}590$). MS (HP): M^+ 260 (100), 231 (74), 115 (31), 91 (31).

2-*Diphenylmethylenenorbornane epoxide* **17**. Compound **16** (5.0 g 19.2 mmol) was added to 5.0 g (28.8 mmol) of *m*-chloroperbenzoic acid (MCPBA) in 70 ml CH_2Cl_2 at 0°. The reaction was stirred for 6.5 h. The soln was then washed 3 times with 15% NaOH, sat NaCl aq and was then dried with $CaCl_2$. Evaporation of the solvent gave a solid which was recrystallized from hexanes to yield **17** (4.0 g) as colourless crystals, m.p. 92–93°. ^{13}C-NMR (20 MHz, $CDCl_3$) δ: 140.4, 139.7, 127.9, 127.7, 127.1, 126.8, 78.3, 68.8, 40.5, 38.4, 37.6, 36.1, 28.0, 23.7. IR (melt): 3060 (w), 3030 (w), 2950 (s), 2870 (m), 1605 (w), 1495 (m), 1450 (m), 1030 (m), 940 (m), 860 (m), 760 (s), 750 (s), 700 (s). MS (HP): M^+ 276 (28), 167 (17), 166 (100), 165 (20), 105 (12), 77 (19).

endo-2-(*Diphenylmethyl*)-2-*methoxynorbornane* **11**. The epoxide **17** (2.0 g, 7.2 mmol) was reduced by adding metal to **14** (*endo*) using conditions similar to those used for the preparation of **9** (*endo* and *exo*). The solvent was 35 ml anhyd ammonia and 10 ml anhyd EtOH. Na metal (0.67 g, 2.9 mmol; cut into small pieces) was added over 2 h. The crude yield after workup was 2.28 g of a mixture of **10** (*endo* and *exo*; 30%) and **14** (*endo* and *exo*; 70%). This mixture was added to a soln of NaH (0.88 g, 37 mmol) in anhyd diethyl ether (40 ml) followed by the addition of Me_2SO_4 (4.6 g, 37 mmol). The reaction was refluxed for 18 h and was then quenched by pouring into water. The aqueous layer was extracted with diethyl ether and the combined organic layers were washed with conc NH_4OH, sat NaCl aq and was then dried with $MgSO_4$. The pale yellow oil (2.1 g), obtained upon evaporation of the solvent, was purified by MPLC. The first compounds to elute were **10** (*endo* and *exo*); followed by **11** (*endo*; 474 mg) and finally 745 mg of the unreacted alcohols **14** (*endo* and *exo*). The yield of **11** (*endo*; m.p. 64–66°) was 60% (based on recovered starting material). ^{1}H-NMR (361.1 MHz, $CDCl_3$) δ: 7.53–7.15 (m, 10H), 4.02 (s, 1H), 2.78 (s, 3H), 2.47 (brs, 1H), 2.25 (brs, 1H), 1.85–1.80 (brd, 1H), 1.73–1.65 (brd, 2H), 1.61–1.42 (m, 2H), 1.29–1.17 (m, 3H). ^{13}C-NMR (20 MHz, $CDCl_3$) δ: 142.7, 142.4, 130.3, 129.9, 129.6, 127.8, 127.7, 125.9, 88.3, 57.0, 52.7, 44.9, 43.3, 37.2, 36.3, 29.2, 23.9. IR (melt): 3060 (w), 3020 (w), 2960 (s), 2870 (m), 2830 (m), 1600 (w), 1490 (s), 1440 (s), 1090 (s), 1060 (m), 1030 (w), 740 (m), 710 (m), 690 (s). UV (hexanes): $\lambda_{max} = 259$

nm (ε = 568). MS (HP): M^+ 292 (0.5), 167 (15), 165 (28), 125 (100), 93 (96). (Found: C, 85.75; H, 8.15. Calc: C, 86.25; H, 8.27%.)

2,2-*Dimethoxynorbornane*. This was produced by the treatment of norcamphor with trimethyl orthoformate/*p*-toluenesulfonic acid in MeOH.[37] The yield of 2,2-dimethoxynorbornane obtained as a colourless liquid was 65%. ^{1}H-NMR (T-60, $CDCl_3$) δ: 3.13 (s, 3H; OCH_3), 3.10 (s, 3H; OCH_3), 2.40–2.10 (m, 2H), 1.77–1.00 (m, 8H). MS (HP): M^+ 156 (40), 115 (100), 101 (74), 91 (38), 59 (72).

Irradiations

All irradiations were followed by GC/MS (HP). Compounds **7**, **8**, **9** (*endo* and *exo*) and **10** (*endo* and *exo*) were irradiated under standard conditions at 10° and 80° and no products resulting from C—C bond cleavage or *endo–exo* isomerization were detected. Compound **9** (*exo*) gave trace quantities of **20** and **21**, these structural assignments are tentative and are based only on GC/MS analysis. The pure products were not isolated. Similar results were obtained for **9** (*endo*) but the reaction was much slower. When **11** (*endo* and *exo*) were irradiated at 10° they rapidly cleaved giving **2** and 2,2-dimethoxynorbornane as the major products. The minor products of this reaction were **5**, norcamphor, 2,3-dimethoxynorbornane and norcamphor methyl enol ether (identified by GC/MS). The minor products were produced in a combined yield of 15%. Compound **6** reacted at both 10° and 80°; the products were **2**, **18** and trace amounts of **5**, **19** and 2,3-dimethyl-2,3-diphenylbutane. These data are summarized in Table 1.

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