The photochemistry of indenyl alcohols and esters: Substituent effects on the competition between ion- and radical-derived products

J.A. Pincock and I.S. Young

Abstract: The photochemistry of the indenyl acetates **1** and pivalates **2**, substituted with X = H, 5-CH_3O, and 6-CH_3O, have been examined in both methanol and cyclohexane. The precursor alcohols **3** were also found to be photoreactive. Although only radical-derived products were obtained in cyclohexane, both ion- and radical-derived products were formed in methanol. The absence of significant fluorescence emission from any of the substrates **1**, **2**, and **3** indicates that the excited singlet states are highly reactive. A mechanism is proposed for the ion-derived products that proceeds through direct heterolytic cleavage to give an indenyl cation – carboxylate anion pair. The indenyl cations generated are anti-aromatic in the ground state and their efficient generation by this photochemical solvolysis is in sharp contrast to the very low reactivity of related ground-state substrates. For the pivalate esters **2**, an excited-state migratory decarboxylation is proposed for the formation of *tert*-butyl derived products.

Key words: ester photochemistry, indenyl cations, indenyl radicals.

Résumé : La photochimie des acétates **1** et des pivalates **2** d'indényle, substitués avec X = H, 5-CH_3O et 6-CH_3O a été étudiée dans le méthanol et dans le cyclohexane. On a trouvé que les alcools précurseurs **3** sont également photoréactifs. Dans le cas du cyclohexane on n'obtient que des produits d'origine radicalaire, par contre dans le cas du méthanol on obtient des produits d'origine ionique et d'origine radicalaire. L'absence d'émission de fluorescence significative à partir des substrats **1**, **2** et **3** indique que les états singulets excités sont hautement réactifs. On propose un mécanisme qui explique la formation des produits d'origine ionique via le clivage hétérolytique direct pour donner une paire cation indényle – anion carboxylate. Les cations indényles générés sont anti aromatiques dans l'état fondamental et leur production efficace par cette solvolyse photochimique est en nette opposition avec la très faible réactivité des substances apparentées à l'état fondamental. Pour les esters pivalates **2**, on propose une décarboxylation migratoire de l'état excité pour expliquer la formation des produits dérivés du *t*-butyle.

Mots clés : photochimie des esters, cations indényles, radicaux indényles.

[Traduit par la Rédaction]

Introduction

The photochemistry of arylmethyl esters ($ArCH_2O$-(CO)-R) in nucleophilic solvents (1) and arylmethyl compounds with leaving groups in general ($ArCH_2$-LG) (2) has recently attracted considerable interest. As outlined in the mechanism in Scheme 1, products are derived from both radical pair and ion pair (photosolvolysis) intermediates and, for esters at least, only from the excited singlet state. Apart from a fundamental interest in the factors (substituents, solvent, leaving group, excited-state multiplicity) that control the partitioning between these two pathways, the potential of applying this process to the design of photolabile protecting groups or phototriggers has been explored (3, 4).

On the basis of extensive studies on a range of functionalized arylmethyl esters, we have proposed a mechanism where the major pathway for reactivity is homolytic cleavage (k_{hom}) of the carbon—oxygen bond to give a radical pair (1, 2). Competition between electron transfer (k_{et}) to form an ion pair and decarboxylation (k_{CO2}) of the acyloxy radical then controls product distribution. This latter process serves as a radical clock with the rate constant differing by many orders of magnitude, depending on the stability of the radical formed. Values range from ~10^6 s^{-1} for $ArCO_2^•$ (5) to ~10^9 s^{-1} for $RCO_2^•$ with primary alkyl groups (6). For cases that form highly stabilized radicals, such as $Ar_2C(OH)CO_2^•$, the decarboxylation occurs within a few picoseconds; the rate constants approach those for barrier-free unimolecular reactions (7). The rate of electron transfer also ranges over several orders of magnitude and follows Marcus theory in both the normal and the inverted region (8, 9). On the basis of high-level MO calculations, this mechanism has been questioned in favor of one involving direct heterolytic cleavage (k_{het}) from S_1, particularly for substrates with *meta*-methoxy substitutents (10, 11).

The high reactivity and the high yield of ion-derived products for the photochemistry of 9-fluorenol in mixed organic–aqueous media has been interpreted as resulting from the formation of a cyclically conjugated 4*n* π cation (12, 13).

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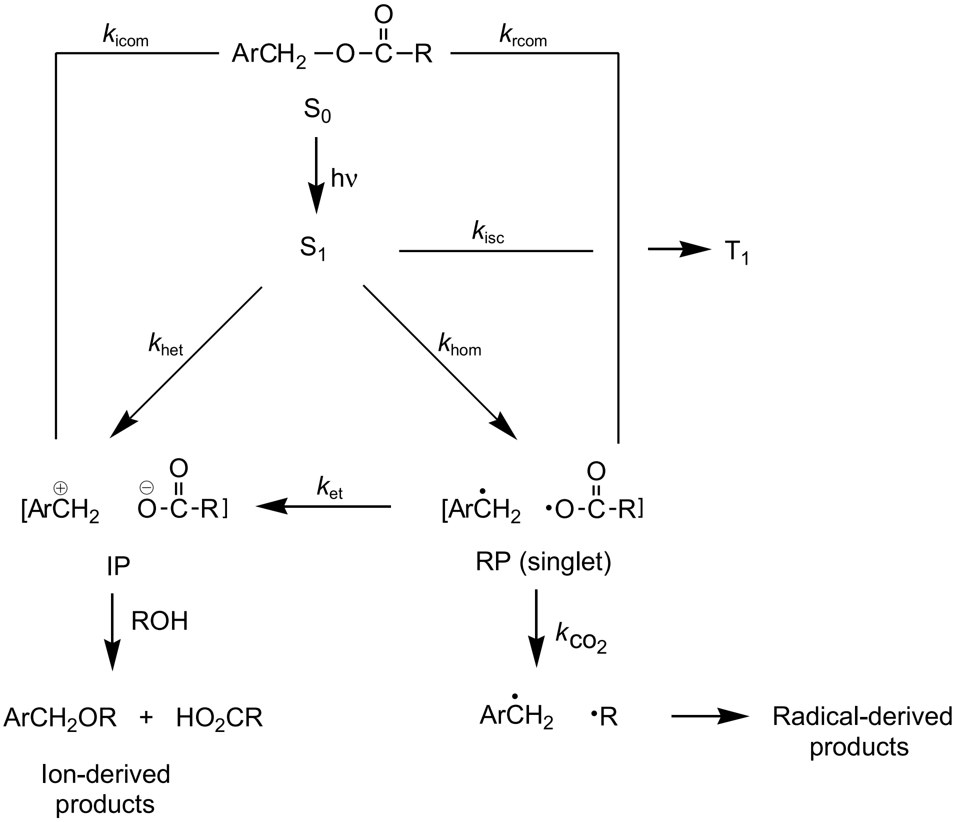
Scheme 1. General mechanistic scheme for the photolysis of benzylic substrates.



Recent picosecond laser flash photolysis (LFP) experiments (14) have shown that in fact 9-fluorenol reacts to form the 9-fluorenol cation very rapidly (<10 ps) in solvents (water, TFE, HFIP) of high polarity (E_T^N). The antiaromatic character of the 9-fluorenyl cation has been discussed in a recent review (15) with the conclusion that it will be attenuated relative to that for cyclopentadienyl and indenyl cations. In fact, on the basis of recent calculations, the fluorenyl cation has been described as nonaromatic by some criteria and antiaromatic by others (16). The possible photochemical generation of indenyl cations, which, from experiment and calculation, have more antiaromatic character than fluorenyl cations, is therefore of interest.

We now report on the photochemistry of six indenyl esters **1a**–**c** and **2a**–**c** and three indenyl alcohols **3a**–**c** in the solvents methanol and cyclohexane. The photochemistry of the alcohols was examined to allow a more direct comparison with the photochemistry of 9-fluorenol. The choice of examining acetate esters **1** vs. pivalates **2** was made because the rate constants of decarboxylation of their corresponding acyloxy radicals differ by an order of magnitude (~10^9 s^{-1} for $CH_3CO_2^{\bullet}$ vs. 1.1×10^{10} s^{-1} for $(CH_3)_3CCO_2^{\bullet}$) (6), and these radicals are good probes for radical pair chemistry. The choice of 5-methoxy vs. 6-methoxy was made in order to examine the effect of the change in position of the electron-donating group from *para* (5-methoxy) in **1b**, **2b**, and **3b** to *meta* (6-methoxy) in **1c**, **2c**, and **3c** relative to the arylmethyl center with the leaving group. The results will also be compared with those obtained previously for the corresponding indanyl derivatives (17).

Results and discussion

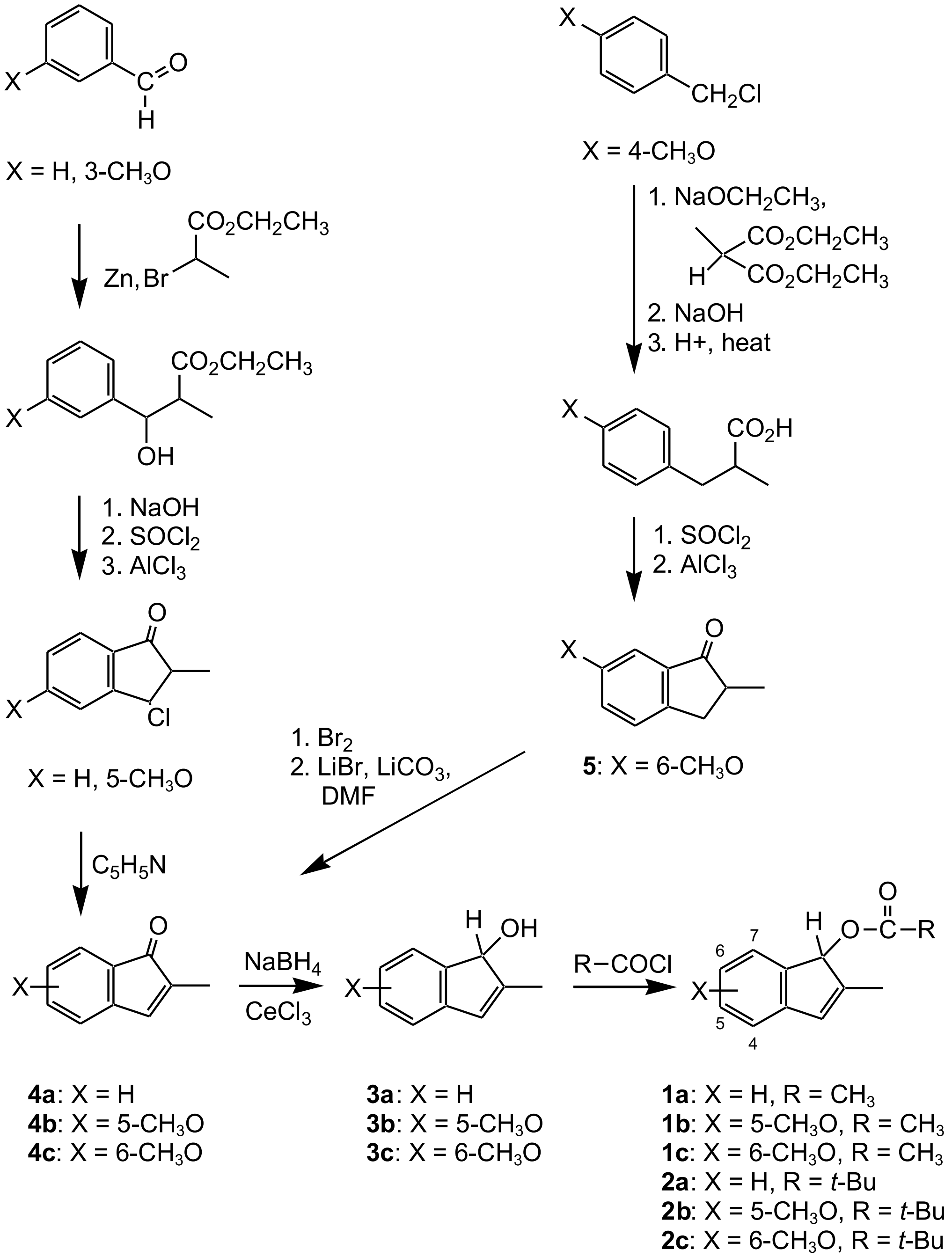
Synthesis of alcohols and esters

The esters were synthesized from the corresponding alcohols **3** by reaction with the appropriate acid chloride in benzene–pyridine, Scheme 2. The alcohols were obtained by reduction of the ketones **4** with $NaBH_4$ with added $CeCl_3$. In the absence of the $CeCl_3$, considerable reduction of the indenone double bond occurred (18). Two of the indenones (**4a**: X = H and **4b**: X = 5-CH_3O) were prepared by a procedure developed by Floyd and Allen (19) and used in our laboratory previously (20). The indanone **5** (X = 6-CH_3O) could not be prepared by this method because the Friedel–Crafts cyclization was not successful. Instead, the method of Sam and Plampin (21) was used. The indenone **4c** (X = 6-CH_3O) was then prepared from **5** by a bromination–dehydrobromination sequence.

Absorption and emission spectra of the esters and alcohols in methanol

In general, indene derivatives have UV absorption spectra with two bands, a weak one ($\epsilon \sim 10^2$ (mol L^{-1})$^{-1}$ cm^{-1}) between 280 and 300 nm, corresponding to the symmetry-forbidden ^1L_b band in benzene, usually partially overlapped by a stronger one ($\epsilon \sim 10^4$ (mol L^{-1})$^{-1}$ cm^{-1}) around 260 nm, corresponding to the symmetry-allowed ^1L_a band in benzene (22). In methanol, the unsubstituted indenyl ester **1a** has two similar bands (λ_{max} = 266 nm, ϵ = 7130 (mol L^{-1})$^{-1}$ cm^{-1} and 306 nm, 391 kJ mol^{-1} (the longest wavelength maximum in the long wavelength band), ϵ = 950 (mol L^{-1})$^{-1}$ cm^{-1}), but

Scheme 2. Synthesis of the esters **1a**–**c** and **2a**–**c** and the alcohols **3a**–**c**.



these are shifted to somewhat longer wavelength than that for 2-methylindene (22) in cyclohexane (λ_{max} = 257 nm, ϵ = 11 700 (mol $L^{-1})^{-1}$ cm^{-1} and 295 nm, ϵ ~ 500 (mol $L^{-1})^{-1}$ cm^{-1}) or *cis*-phenylpropene (23) in hexane (λ_{max} = 256 and 288 nm). The long wavelength band has a series of obvious, but broad, vibrational bands in contrast to the shorter wavelength band, which does not. The methoxy-substituted esters **1b** and **1c** have similar absorption bands (see Experimental section), although the long wavelength band lacks vibrational structure and moves to even lower energy (320 nm, 373 kJ mol^{-1}) for the 6-methoxy isomer **1c**, as expected when compared with a similar shift to longer wavelength for *trans*-1-(4-methoxyphenyl)propene (λ_{max} = 298 nm) relative to *trans*-1-phenylpropene itself (λ_{max} = 284 nm) (23).

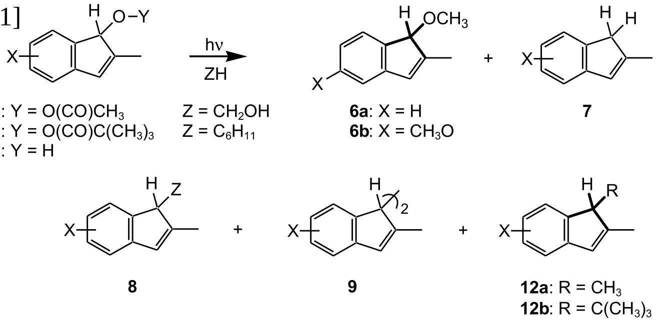
Fluorescence spectra for the three indenyl esters **1** in methanol revealed only extremely weak, if any, emission. The quantum yields of emission were estimated to be less than 0.001 when compared with that for naphthalene (0.21). The alcohols **3**, precursors for the esters, also did not fluoresce significantly. In contrast, 3-methylindene, which is photochemically unreactive in hexane, has a quantum yield of fluorescence of 0.077 and excited singlet state lifetimes of 13.9 ns (22); the major process competing with fluorescence from the excited singlet state is likely intersystem crossing.

The very inefficient fluorescence for the indenyl compounds studied here strongly suggests that they are undergoing rapid ($k > 10^9$ s^{-1}) excited-state cleavage of the indenyl C1 to oxygen bond. The absence of measurable fluorescence unfortunately prevents the determination of excited-state lifetimes and rate constants for excited-state processes.

Photochemistry of the alcohols 3 in methanol and cyclohexane

The photolysis of the indenyl alcohols in either methanol or cyclohexane gave the products expected from arylmethyl photochemistry, as shown, in a general way, in eq. [1].[2]

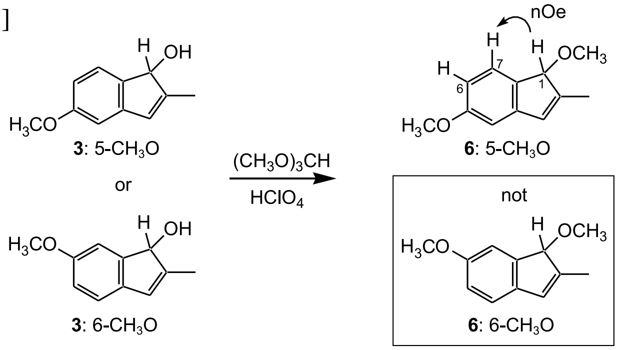
[1]



The methyl ethers **6**, formed only in methanol, are of particular interest because they are clearly derived from indenyl cations. The hydrocarbon products **7**–**9** are radical derived. The reactions are relatively efficient; irradiation of 60 mg of **3a** (X = H) in 100 mL of methanol with 254 nm lamps in a Rayonet reactor resulted in 72% conversion in 15 min. The difficulties in completely characterizing the photoproducts of these reactions can be exemplified by this case. At this extent of conversion, the mass balance (GC peak areas) was only 60%. This is characteristic of the photochemistry of indene derivatives where quantum yields for disappearance of starting material are often considerably higher than those for appearance of volatile products (24), presumably as a consequence of oligomerization processes. Moreover, complete separation by flash or radial chromatography of the non-polar hydrocarbon products was not possible. GC–MS analysis of mixtures of variable composition was invaluable for preliminary structural assignment. For the unsubstituted substrate, **3a**, the hydrocarbons **7** (X = H) (commercial sample, Aldrich) and the dimers **9** (X = H) (*meso* and *dl* diastereomers) are known (25, 26), and literature ^{1}H NMR spectra were helpful in identifying components in the mixtures obtained by chromatography.

The methyl ethers **6** were synthesized from the indenols **3** using trimethyl orthoformate under acidic conditions (aqueous $HClO_4$) (27). An attempt to alkylate **3a** (X = H) using NaH–DMSO followed by CH_3I resulted in 2,2-dimethylindanone, confirming that the indenyl hydrogen at C1 is more acidic (pK_a = 20) than an alcohol (pK_a [CH_3OH] = 29) in DMSO (28). Using the trimethyl orthoformate procedure for the indenols **3b** (X = 5-OCH_3) and **3c** (X = 6-OCH_3) resulted in the isolation of only one ether independent of which alcohol was used as the starting material, eq. [2].

[2]



The compound obtained was shown to be the 5-methoxy isomer, **6b**, by NOE difference spectra: irradiation of H1 (δ = 4.82 ppm) gave a strong enhancement for H7, which is assigned by its higher chemical shift (δ = 7.30 ppm) relative to that of H6 (δ = 6.64 ppm) for the two aromatic protons, which are *ortho* to each other and therefore have a coupling constant of 8.0 Hz. This acid-catalyzed reaction, which presumably proceeds through the indenyl cation, raises an interesting point for reactions that generate indenyl cations or radicals at C1 of the 5-methoxy and 6-methoxy substrates. Because of delocalization through C1, C2, and C3 of these intermediates, both substrates will generate the same intermediate for either the cation **10** or the radical **11**, Fig. 1.

This observation prompted us to examine the charge and spin distribution in these species by PM3 calculations.[3] As shown in Fig. 1*a*, nine resonance forms can be drawn for an indenyl cation with a positive charge on each one of the nine carbons. From the calculations for the indenyl cation (C_{2v} symmetry), the positive charge is mainly on C1 and C3 (+0.34 for each, 0.68 total, with hydrogen charges summed into the carbons), as indicated by the first two resonance forms. This suggests that, to a first approximation, the indenyl cation can be viewed as an allyl cation fused to a benzene ring. For 5-substituted indenyl cations, the C_{2v} symmetry is no longer present. For these preliminary calculations, as shown in Fig. 1*b*, we chose the substituent as OH to model the OCH_3 group in order to minimize conformational complications. For the radical, the spin population at C1 (0.89) and C3 (0.72) is similar and delocalization results in a structure with similar bond lengths in the upper and lower part, i.e., the OH group only slightly perturbs the plane passing through C2 and bisecting the C5—C6 bond. In contrast, the calculations of the atomic charge density for the cation reveal a much higher positive charge at C1 (+0.21) than C3 (–0.03); values for C1 (+0.44) and C3 (+0.25) are obtained with hydrogen charges summed into the carbons. In addition, the bond lengths indicate that the indenyl ring system can be pictured as almost two independent π-systems. The first, a 5-hydroxy pentadienyl cation for the string of carbons from C1 through the ring fusion to C7, C6, and C5, with almost equal bond lengths (1.41 ± 0.02 Å) and the sec-

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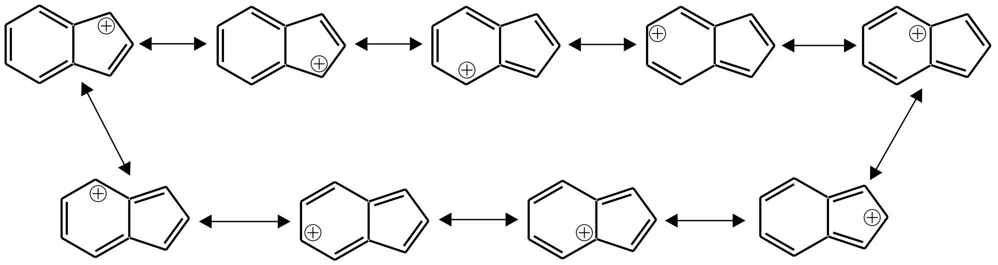
[2] The products **12** in eq. [1] cannot be formed from the alcohols **3** but only from the esters **1** and **2**, as will be discussed later.

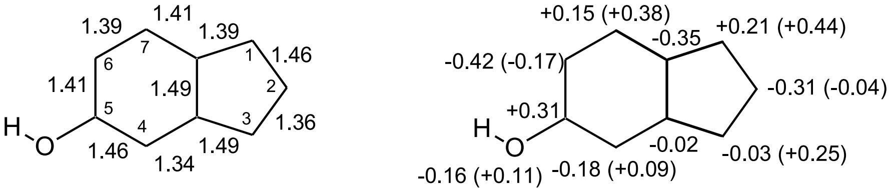
[3] We thank Dr. F. Ban, Dalhousie University, Department of Chemistry, Halifax, Nova Scotia, for these calculations.

Fig. 1. (*a*) Resonance structures for the indenyl cation and (*b*) bond lengths (Å), atomic charges, and spin densities for the 5-hydroxy-1-indenyl cation and radical. Values in brackets for the cation have the charge for the hydrogen atom summed into the value for the carbon.

1a

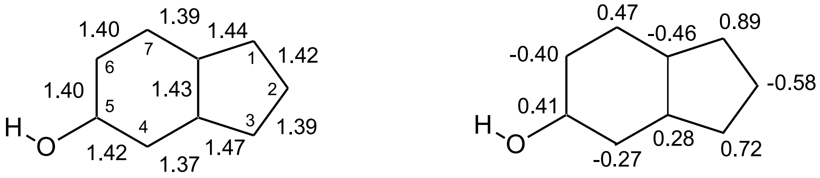


1b



10 (cation): bond lengths

10 (cation): charges



11 (radical): bond lengths

11 (radical): spin densities

ond, an isolated butadiene fragment from C2 to C4 with alternating short (~1.35 Å) and long (1.49 Å) bond lengths; i.e., the OH group severely perturbs the structure on either side of the same plane (defined above) for the radical. The high positive charge density at C1 of the cation, which was obtained from these calculations, rationalizes nicely why both indenols **3** (X = 5-OCH_3 and X = 6-OCH_3) give the same ether **6** (X = 5-OCH_3) in the synthesis, eq. [2], and in the photochemistry, eq. [1]. The calculations for the hydroxyindenyl radical **10** will also be relevant to the photolysis results described below. Higher level MO calculations on the charge and spin distribution in substituted indenyl cations and radicals are in progress.

Another issue in the photolysis experiments was that of secondary photochemistry of several kinds. First, alkyl indenes are well known to photoisomerize (24). For instance, 2-methylindene **7** (X = H) isomerizes to both 1- and 3-methylindene (Φ = 0.13) on photolysis in hexane and even isomerizes to 2-methyleneindane under acidic conditions (29). Similarly, 1,2-dimethylindene **12a** (X = H, R = CH_3) isomerizes to the 2,3-isomer (24). We have confirmed these previous observations by the photolysis of 2-methylindene in methanol, which gave three isomers (GC–MS) along with 2-methoxy-2-methylindane by *anti*-Markovnikov addition of methanol, also as reported previously (30). In agreement with these observations, at higher conversions, the initially formed products decreased in yield as the other isomers appeared (GC–MS). Second, photolysis in methanol of the

Table 1. Product yields for the photolysis of the alcohols **3** in cylohexane and methanol.

	X	Solvent	% Con (t)^a	**6**	**7**^{b}	**8**^{b}	**9**^{c}
3a	H	CH_3OH	27 (5)	7	7	35	50 (1:1.2)
3a	H	C_6H_{12}	30 (5)	—	15	60	25 (1:1.2)
3b	5-CH_3O	CH_3OH	21 (2)	80	20 (1:1.2)	—	—
3b	5-CH_3O	C_6H_{12}	58 (5)	—	10 (1:1.6)	90 (1:1.3)	—
3c	6-CH_3O	CH_3OH	12 (2)^d	80	20 (1:1.5)	—	—
3c	6-CH_3O	C_6H_{12}	18 (5)^e	—	10 (1:1.4)	90 (1:1.1)	—

Note: Yields are normalized to 100%. Estimated error ±5%.

[a] Percent conversion (photolysis time) for ~50 mg of substrate in 100 mL of solvent.

[b] Numbers in brackets refer to the ratio of the two possible regioisomers.

[c] Numbers in brackets refer to the ratio of the two possible diastereomers.

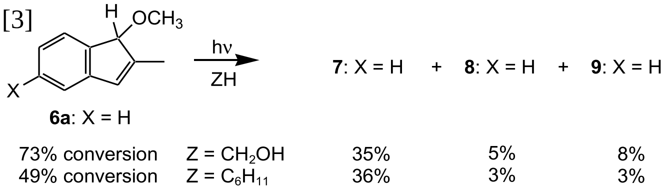
[d] Ratio of **3c**:**3b** = 12:1 at this percent conversion.

[e] Ratio of **3c**:**3b** = 7.8:1 at this percent conversion.

ether **6a** (X = H), the ion-derived product, resulted in formation of the radical-derived products **7**, **8**, and **9**, eq. [3].

The major product in this photolysis, 2-methylindene **7** (X = H), is probably derived by disproportionation of the indenyl–methoxy radical pair, as proposed previously for the photolysis of 9-methoxyfluorene derivatives (12, 13). Third, as indicated in Table 1, the 6-methoxy alcohol **3c** converts photochemically to the 5-methoxy isomer **3b**. For instance, at 14% conversion in cyclohexane, the ratio of **3c**:**3b** was 7.8:1. As a consequence of these various secondary photochemistries, only product yields obtained at low conversions (<5%) give values that are useful for mechanistic consideration. These values are given in Table 1. Because the percentage conversion is too small to reliably determine the mass balance, the yields are normalized to 100%.

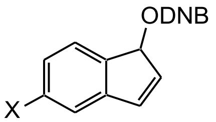
[3]



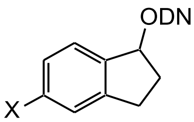
The products shown in eq. [1] and Table 1 for the photolysis of the alcohols **3** are easily explained by formation of indenyl radical and cation intermediates. A mechanism is outlined in Scheme 3, a specific example of the general Scheme 1. The most interesting observation is the very high yield in methanol of the ion-derived product, the methyl ester **6**, particularly from the methoxy-substituted substrates **3b** and **3c** (82%). Also, the same product yields are obtained for both substrates **3b** and **3c**, indicating that both the indenyl radical and cation lose, as expected, the memory of the substrate from which they originated. The radical-derived products **7** and **8** from **3b** and **3c** are mixtures (ratio ~ 1.3:1) of two regioisomers, as expected for the unequal spin distribution at C1 and C3 for the methoxy-substituted indenyl radical. The formation of these products is rationalized (Scheme 3) by exothermic hydrogen abstraction (31) by the hydroxyl radical from the solvents methanol (bond dissociation energy (BDE) = 393 kJ mol^{-1}) and cyclohexane (BDE= 401 kJ mol^{-1}) to give water (BDE = 497 kJ mol^{-1}) and the hydroxymethyl and cyclohexyl radical, respectively. The indenyl radical will not abstract a hydrogen atom from these solvents because the process would not be exothermic (BDE = 351 kJ mol^{-1} for the C1—H bond in indene). Reaction of the two radicals by disproportionation then gives **7**, whereas coupling gives **8**, in a ratio of 1:9 in cyclohexane. In methanol, only disproportionation was observed. The other major products that are radical derived are the two indenyl dimers, **9** (X = H), now diasteromers (*dl* and *meso*) because regioisomers are not possible. For reasons that are not obvious, similar dimers were not observed for the methoxy-substituted substrates.

The major conclusion from these results is that indenyl cations are efficiently formed in the photochemistry of indenyl alcohols. Similar cations have been generated by ground-state solvolysis of the indenyl compounds **13**, and rate retardations of approximately 10^{-5} have been measured relative to the corresponding indanes **14** in 80% aqueous acetone, reflecting the antiaromatic destabilization of the cation derived by solvolysis of **13** (32).

Product studies indicated that two regioisomeric alcohols are formed from both **13** (X = CH_3) and **13** (X = CH_3O), although the experimental evidence for the latter compound is not conclusive. Moreover, these solvolysis reactions were carried out at high temperature (100 °C for 22 days), conditions where 5- and 6-substituted indene derivatives may be equilibrating thermally by 1,5-hydrogen migrations involving isoindene derivatives (33). The question as to whether the ion pair is generated by direct heterolytic cleavage (k_{het}, Scheme l) or by electron transfer from an initially formed radical pair (k_{et}) cannot be answered from these results. However, the clear evidence from LFP experiments for direct heterolytic cleavage to the ion pair for 9-fluorenol in polar protic solvents (14) suggests that the first pathway is possible. Moreover, the very high oxidation potential expected for the indenyl radical makes the latter seem unlikely. Therefore, the efficient photochemical formation of the indenyl cations (Scheme 3) would seem to be another exam-



13



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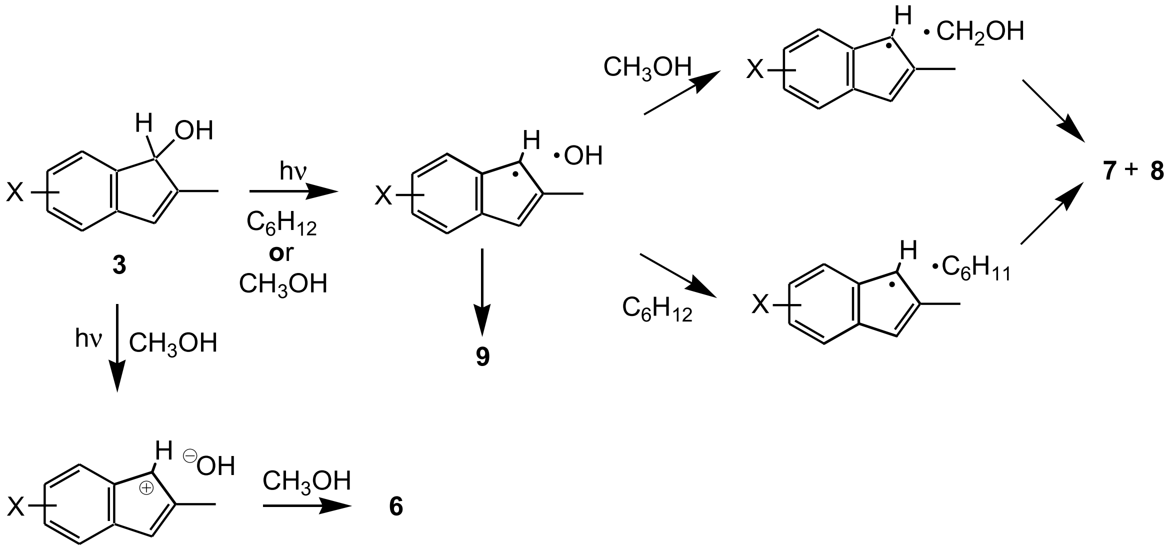
Scheme 3. Mechanistic pathways for the photolysis of the alcohols **3a**–**c** in methanol and cyclohexane.



ple of the generation of a 4*n* π cation, first proposed by Wan and co-workers for the photodehydroxylation of fluorenol (12, 13).

Photochemistry of the esters 1 and 2 in methanol and cyclohexane

The photolysis of the indenyl esters **1** and **2** in either methanol or cyclohexane again gave the products expected from arylmethyl photochemistry, also shown in eq. [1]. Again, the reactions are relatively efficient; irradiation of 100 mg of **1a** (X = H, R = CH_3) in 100 mL of methanol with 254 nm lamps in a Rayonet reactor resulted in 50% conversion in 15 min. The same difficulties as for the alcohols **3** (lack of separation of non-polar products and secondary photochemistry) were encountered in completely characterizing the photoproducts for the esters. Moreover, an additional secondary photochemical process was revealed, involving the coupling products **12b** (R = $C(CH_3)_3$). The ratio of these two *tert*-butyl products derived from the 5- and 6-methoxy pivalate esters changed with the percent conversion. Parallel to this process, the yield of the two isomeric 5- and 6-methoxy-2-methylindene derivatives **7** increased. For instance, the yield of **7** for photolysis of the pivalates **2b** and **2c** in methanol was essentially zero at very low conversion (<5%) but reached 20–25% at high conversion (>80%). Finally, the 6-methoxy esters **1c** and **2c** were converted to the corresponding 5-methoxy substrate **1b** and **2b** (see footnotes in Tables 2 and 3). This observation is expected on the basis of the internal return processes (k_{icom} and k_{rcom}, Scheme 1) previously observed for the intermediates in ester photochemistry (34–36). Again as a consequence of these competing processes, only product yields obtained at very low conversions (<5%) are useful for mechanistic consideration. These values are given in Table 2 for reactions in cyclohexane and in Table 3 for those in methanol. Because the percentage conversion is too small to determine reliably, the yields are normalized to 100%.

Table 2. Product yields for the photolysis of the esters **1** and **2** in cyclohexane.

	X	R	**7**[a]	**9**[a]	**12**[b]
1a[c]	H	CH_3	—	15 (1:1.3)	80
2a	H	$(CH_3)_3C$	20	15 (1:1.3)	65
1b	5-CH_3O	CH_3	—	—	100 (1:2.3)
2b	5-CH_3O	$(CH_3)_3C$	15 (1:1.1)	—	85 (1:2.5)
1c[d]	6-CH_3O	CH_3	—	—	100 (1:1.5)
2c[e]	6-CH_3O	$(CH_3)_3C$	25 (1:1.1)	—	75 (1:2.1)

Note: Yields are for low conversion (<10%) and normalized to 100%. Estimated error ±5%.

[a] Numbers in brackets refer to the ratio of the two possible diastereomers.

[b] Numbers in brackets refer to the ratio of the two possible regioisomers.

[c] For **1a**, 8% of the material was 1-cyclohexyl-2-methylindene **8**, a product not detected for the other five compounds.

[d] Ratio of **1c**:**1b** = 5.8:1 at 41% conversion.

[e] Ratio of **2c**:**2b** = 3.9:1 at 75% conversion.

The photolysis products obtained for the esters **1** and **2** in cyclohexane are easily explained by the radical pair mechanism in Scheme 4, where the radical paired with the indenyl one is now an acyloxy, rather than hydroxyl as it was for the indenols in Scheme 3. For the acetates **1** (R = CH_3), decarboxylation gives the methyl radical leading to the coupling product **12a** (R = CH_3) (two regioisomers for X = 5-CH_3O and 6-CH_3O). For the pivalates **2** (R = $C(CH_3)_3$), decarboxylation now gives the *tert*-butyl radical, leading to the coupling product **12b** (R = $C(CH_3)_3$) and disproportionation to 2-methylindene **7** (again, two regioisomers for X = 5- and 6-CH_3O for both **7** and **12b**). As in the photolysis of the indenols **3** (Table 1), the out-of-cage dimers were only obtained for the unsubstituted esters **1a** and **1b**. The very similar yields of **7** and **12** obtained for both the 5- and 6-methoxy substrates, independent of which one is the starting material, indicates that the indenyl radical again loses the memory of its precursor.

The products obtained for the photolysis of the indenyl esters in methanol are given in Table 3. Particularly striking is the very high yield of the ion-derived product, the methyl ether **6**, particularly from the 5- and 6-methoxy acetates, **1b**

Table 3. Product yields for the photolysis of the esters **1** and **2** in methanol.

	X	R	**6**	**7**	**9**[a]	**12**[b]	Ion:radical[c]	Ion:radical[d]
1a	H	CH_3	15	—	25 (1:1.4)	60	0.18:1	1.4:1
2a	H	$(CH_3)_3C$	—	10	20 (1:1.2)	70	<0.02:1	0.21:1
1b	5-CH_3O	CH_3	75	—	—	25 (1:2.1)	3.0:1	0.10:1
2b	5-CH_3O	$(CH_3)_3C$	20	—	—	80 (1:1.6)	0.25:1	<0.02:1
1c[e]	6-CH_3O	CH_3	100	—	—	—	>50:1	2.3:1
2c[f]	6-CH_3O	$(CH_3)_3C$	30	—	—	70 (1:1.2)	0.33:1	0.25:1

Note: Yields are for low conversion (<5%) and normalized to 100%. Estimated error ±5%.

[a] Numbers in brackets refer to the ratio of the two diastereomers.

[b] Numbers in brackets refer to the ratio of the two possible regioisomers.

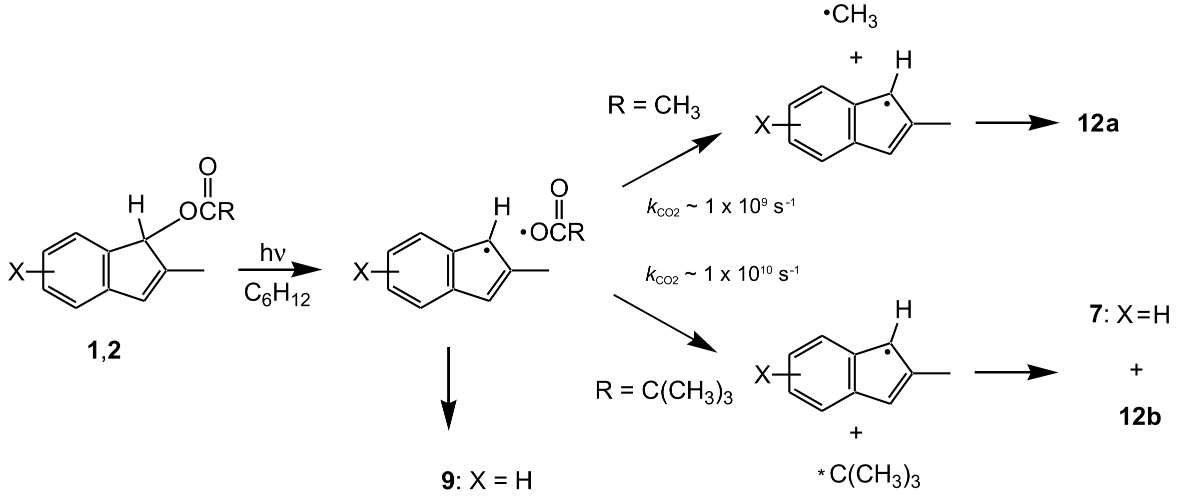
[c] Ratio of ion- to radical-derived products for the indenyl esters **1** and **2**.

[d] Ratio of ion- to radical-derived products for the analogous indanyl esters, **15** and **16**, ref. 17.

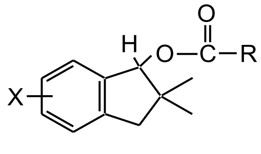
[e] Ratio of **1c**:**1b** = 8.7:1 at 48% conversion.

[f] Ratio of **2c**:**2b** = 40:1 at 32% conversion.

Scheme 4. Mechanistic pathways for the photolysis of the esters **1a**–**c** and **2a**–**c** in cyclohexane.



and **1c**. The ratio of ion- to radical-derived product is significantly larger for the methoxy-substituted substrates than the corresponding indanyl (Table 3) derivatives **15** and **16** (17). In fact, the ion-derived ether **6b** (X = 5-CH_3O) is the only product observed (at low conversion) for the acetate **1c** (X = 6-CH_3O). The change in product distribution for the change in substrate from acetate esters **1** to pivalate esters **2** has been used effectively in the past by us (1) and others (37) to test for the intervention of acyloxy radicals. Their very different rates of decarboxylation serve as radical clocks for other possible processes of the radical, in particular, the electron transfer process (k_{et}, Scheme 1) that converts the radical pair to the ion pair.

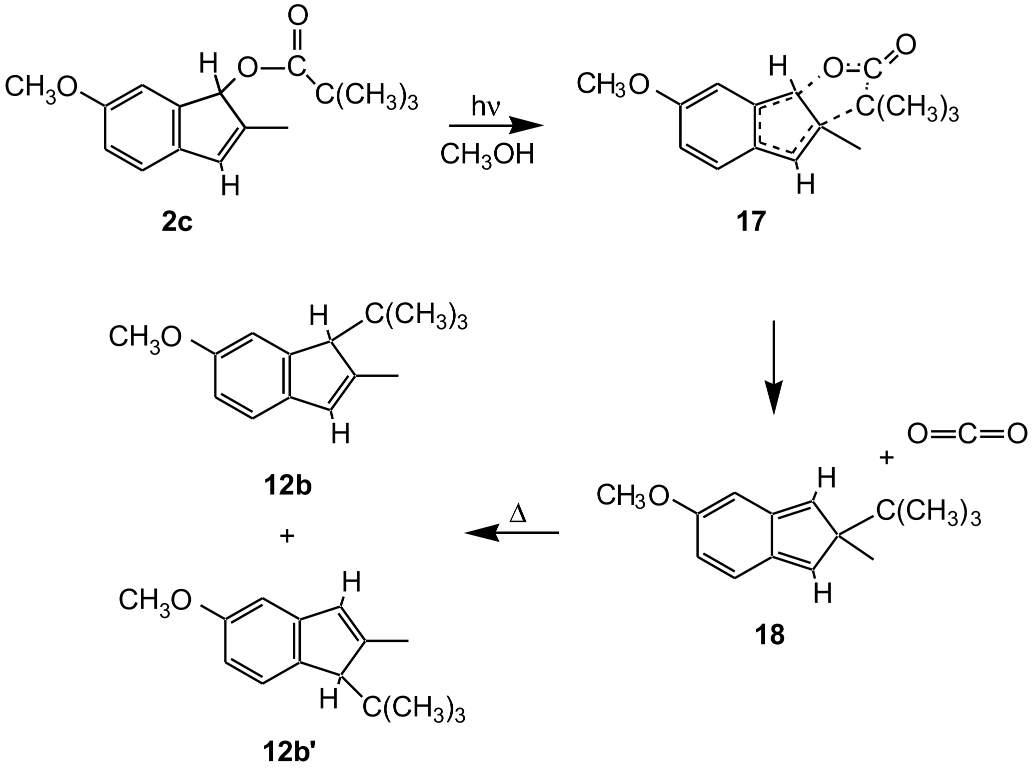


15: R = CH_3
16: R = $C(CH_3)_3$

However, the surprising observation of the absence of the disproportionation products **7** in the photolysis of the 5- and 6-methoxy pivalates esters **2b** and **2c** at low conversion in methanol suggests that free *tert*-butyl radicals are not formed. This observation emphasizes why product yields at low conversion are essential for understanding the photochemistry involved. As mentioned above, the yield of **7** increases with the extent of conversion by a process of secondary photochemistry involving **12b** (X = $C(CH_3)_3$). The parallel change in the ratio of the two regioisomeric coupling products **12** indicates that this secondary photochemistry is homolytic carbon—carbon bond cleavage to generate the indenyl–*tert*-butyl radical pair, allowing for both disproportionation and regioisomeric equilibration to occur.

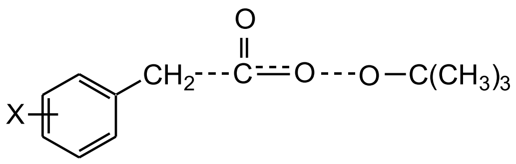
The question then arises as to the mechanism of formation of the *tert*-butyl coupling products if *tert*-butyl radicals are not involved in the primary photochemistry of the methoxy pivalate esters in methanol. A tentative proposal is an excited-state migratory (from C1 to C2) decarboxylation of the *tert*-butyl group via a five-membered transition state **17** (shown in Scheme 5 for the 6-methoxypivalate **2c**) to form an isoindene derivative **18**. Excited state migrations from C1 to C2 are well known for phenyl-substituted indenes (38). The resulting isoindenes would be thermally unstable and revert to indene. On the basis of migratory aptitudes (CH_3 <

Scheme 5. Proposed mechanism for the formation of the coupling products **12** and **12′** for the photolysis of the ester **2c** in methanol.



CH_2CH_3 < $CH(CH_3)_2$) previously determined (33) for the thermal reversion of isoindenes to indenes, the *tert*-butyl group in **18** will migrate in preference to methyl, giving the two observed regioisomeric products, **12b** and **12b′**. The process described by transition state **17** is not observed and not possible for other benzylic substrates, which lack the required indenyl type conjugation. In those cases, disproportionation always accompanies coupling of *tert*-butyl radicals, as expected (39).

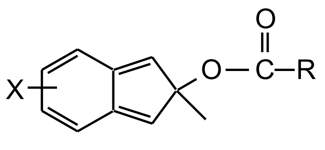
This process is reminiscent of that proposed for the thermal decomposition of peresters, which are concerted (40, 41), where the potential acyloxy radical will fragment very rapidly because of the stability of the radical generated, **19**. These reactions have negative ρ values (approximately –1.1), indicating that the transition states have some positive character on carbon and negative on oxygen (42). The photochemical migration suggested by structure **17** in Scheme 5 might also have a substituent effect, which could potentially explain why the yield of the isomers **12** are slightly different for the 5-methoxy **2b** (80%) vs. the 6-methoxy (70%) pivalate ester **3b**. The substitutent effect could also rationalize why the unsubstituted substrate **2a** seems to undergo normal homolytic bond cleavage and give both coupling (**12**) and disproportionation (**7**) products.



19

The mechanistic proposals for the indenyl esters can then be summarized as follows: In cyclohexane, all three esters react by homolytic cleavage to give radical-derived products as shown in Scheme 4. In methanol, as outlined in Scheme 6, the unsubstituted esters **1a** and **2a** react by the same mechanism for the radical-derived products, but now formation of the ion pair leads to low yields (15%) of the methoxy ether **6** for the acetate **1a**. The decrease in the yield of **6**, as a consequence of the change from acetate **1a** to pivalate **2a**, suggests that the radical clock method is operative and that the ion pair is formed (at least partially) from the radical pair by redox electron transfer (k_{et}, Scheme 1) in competition with the rate of decarboxylation, which is faster by an order of magnitude for the $(CH_3)_3CCO_2$ radical.

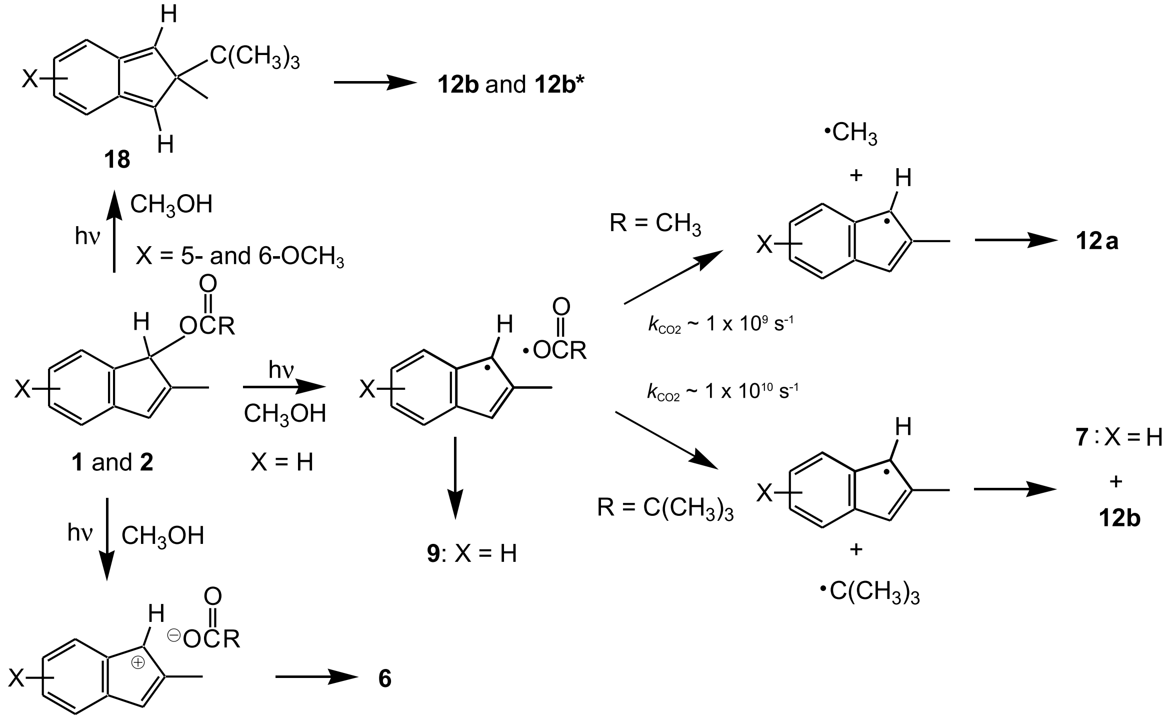
Two other potential photochemically generated intermediates that have not yet been discussed should be mentioned as possible precursors for the ion-derived ether product in methanol. The first, **20**, an isoindene, would result from migration of the acyloxy group from C1 to C2 of the indene.



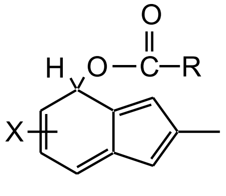
20

The second, **21**, analogous to the intermediate **22** observed in the photolysis of 3,5-dimethoxybenzyl acetate in methanol and other alcohol solvents (43), would be formed by acyloxy migration from C1 to C7. A similar intermediate has been reported for the photolysis of 9-fluorenol in metha-

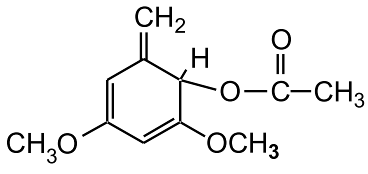
Scheme 6. Mechanistic pathways for the photolysis of the esters **1a**–**c** and **2a**–**c** in methanol.



nol (44) and non-acidic zeolites (45). Either of these could be very reactive (thermally or photochemically) in methanol as solvent. For instance, the half life for ground-state solvolysis of **22** in methanol is approximately 2 min. We are currently conducting nanosecond laser flash photolysis experiments to examine the reactive intermediates for the photochemistry described above.



21



22

Conclusions

For the 5- and 6-methoxy-substituted esters in methanol, the proposed mechanism is that direct heterolytic cleavage from the excited state to form an ion pair (Scheme 6) competes with migratory decarboxylation of the ester to give the isoindene derivative **18** (as shown in Scheme 5). This latter process is less important for the acetates **1b** and **1c** than the pivalates **2b** and **2c**, and therefore, the acetates give very high yields of the ion-derived ether **6**, reaching 100% for the 6-methoxy acetate **1c**! This substrate has the activating group *meta* to the reactive benzylic centre. The photochemical "*meta* effect", as originally proposed by Zimmerman and co-workers (46) for methoxy-substituted benzylic acetates and supported by studies of methoxy-substituted benzylic alcohols by Wan and co-workers (47), predicts enhanced efficiency for heterolytic cleavage reactions for leaving groups *meta* (and *ortho*) to electron-donating substituents. It seems to be playing an important role in the photochemistry of these indenyl esters. This suggestion is in marked contrast to our proposal for all previously studied ester substrates where homolytic cleavage followed by electron transfer is considered to be the dominant mechanistic pathway for the formation of ion-derived products. Although the limited data available make these mechanistic conclusions somewhat speculative, the fact that products derived from indenyl cations are formed in these photoreactions is certain. This may well be a consequence of the antiaromatic character of these 4*n* π cations, in agreement with Wan and co-workers' proposal for 9-fluorenyl derivatives (12, 13).

Experimental section

General procedures

Proton (^{1}H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectra were obtained in $CDCl_3$ on an AC 250 F NMR spectrometer in automation mode. Ultraviolet (UV) spectra were obtained in 1 cm quartz cuvettes on a Varian-Cary Bio 100 spectrometer. Fluorescence measurements were done in methanol, with non-degassed samples, using a PTI spectrometer at 25 °C. Corrected spectra were obtained. GC–MS analyses were performed on a PerkinElmer Autosystem XL instrument with a mass selective detector. The column used was a Supelco 30 m × 0.25 mm MDN-5S 5% phenyl methylsiloxane, film thickness 0.50 μm, temperature programmed: 60 °C for 1 min; 20 °C increase per min to 240 °C; 240 °C for 10 min. GC–FID analyses were done in a similar way except on a Supelco DB200 column. Mass spectral data are reported in units of mass over charge (*m*/*z*) for all values between 50 and the molecular ion if greater than 10% of the base peak. Intensities are reported as a percent of the base peak.

Indenone synthesis

2-Methyl-1-indenone 4a and 5-methoxy-2-methyl-1-indenone 4b

These indenones were prepared using the procedure of Floyd and Allen (), outlined in Scheme 2.

6-Methoxy-2-methyl-1-indenone 4c

The precursor to this indenone, 6-methoxy-2-methyl-1-indanone **5** (X = 6-CH_3O), was prepared using the procedure of Sam and Plampin (), outlined in Scheme 2. To a solution of 13.9 g (79 mmol) of **5** (X = 6-CH_3O) in 170 mL of CCl_4 was added 14.4 g (90 mmol) of bromine in 70 mL of CCl_4. After the addition was complete, the mixture was stirred at room temperature for 2 h. The solvent and excess bromine were removed under reduced pressure and 20.5 g (79 mmol, 100%) of the crude bromide, as a brown solid, resulted. ^1H NMR ($CDCl_3$) δ: 7.22–7.32 (m, 3H), 3.85 (s, 3H), 3.72 (d, 1H, *J* = 18 Hz), 3.41 (d, 1H, *J* = 18 Hz), 1.95 (s, 3H). ^{13}C NMR ($CDCl_3$) δ: 200.4, 160.0, 141.8, 133.8, 127.1, 125.3, 106.7, 60.3, 55.7, 45.8, 27.0. GC–MS: 256 (19), 254 (18), 176 (58), 175 (100), 174 (22), 161 (96), 148 (20), 147 (41), 146 (10), 133 (29), 132 (23), 131 (41), 117 (16), 115 (32), 105 (10), 104 (11), 103 (42), 102 (14), 91 (36), 89 (14), 79 (19), 78 (29), 77 (77), 76 (18), 75 (17), 74 (20), 65 (13), 64 (10), 63 (45), 62 (15), 51 (34), 50 (13). HR-MS calcd. for $C_{11}H_{11}O_2Br$: 253.9942; found: 253.9934. A mixture of 20.5 g (79 mmol) of crude bromoindanone, 12.1 g (139 mmol) LiBr, and 10.4 g (140 mmol) Li_2CO_3 in 175 mL of DMF was heated between 135–140 °C for 3 h under a nitrogen atmosphere. After cooling, the mixture was poured into 300 mL of water and extracted three times with ether. The combined ether layers were washed twice with water and dried with $MgSO_4$. Evaporation of the ether produced 10.4 g of thick red oil that contained crystals. This material was purified by flash chromatography on silica gel producing 3.60 g (21 mmol, 26%) of bright orange needles: mp 82–84 °C. ^1H NMR ($CDCl_3$) δ: 7.06 (q, 1H, *J* = 1.8 Hz), 6.97 (d, 1H, *J* = 2.4 Hz), 6.78 (d, 1H, *J* = 7.9), 6.67 (dd, 1H, J_1 = 2.4, J_2 = 7.9 Hz), 3.77 (s, 3H), 1.81 (d, 3H, *J* = 1.8 Hz). ^{13}C NMR ($CDCl_3$) δ: 198.6, 160.1, 144.1, 136.6, 134.9, 132.7, 121.6, 116.1, 110.9, 55.6, 10.0. GC–MS: 175 (12), 174 (100), 159 (40), 131 (92), 115 (10), 103 (74), 102 (21), 77 (64), 76 (21), 75 (20), 63 (25), 62 (12), 51 (18). HR-MS calcd. for $C_{11}H_{10}O_2$: 174.0681; found: 174.0675.

Indenol syntheses

Indenols **3** were prepared from the corresponding indenones using Luche's reagent (18). The yields were 60–95%.

2-Methyl-1-indenol 3a

mp 84–86 °C. ^1H NMR ($CDCl_3$) δ: 7.09–7.50 (m, 4H), 6.33 (broad s, 1H), 4.84 (broad s, 1H), 2.07 (broad s, 3H), 1.66 (broad s, 1H). ^{13}C NMR ($CDCl_3$) δ: 148.3, 145.2, 143.0, 128.5, 127.0, 124.9, 123.3, 120.1, 78.9, 13.8. GC–MS: 146 (86), 145 (38), 132 (10), 131 (100), 129 (13), 128 (22), 127 (14), 117 (15), 116 (11), 115 (46), 103 (31), 91 (14), 89 (10), 77 (21), 63 (16), 51 (15). HR-MS calcd. for $C_{10}H_{10}O$: 146.0731; found: 146.0741.

5-Methoxy-2-methyl-1-indenol 3b

mp 77–78 °C. ^1H NMR ($CDCl_3$) δ: 7.32 (d, 1H, *J* = 7.9 Hz), 6.68 (d, 1H, *J* = 2.3 Hz), 6.61 (dd, 1H, J_1 = 7.9, J_2 = 2.3 Hz), 6.27 (s, 1H), 4.78 (broad s, 1H), 3.79 (s, 3H), 2.05 (broad s, 3H), 1.64 (broad s, 1H). ^{13}C NMR ($CDCl_3$) δ: 160.3, 149.9, 144.74, 137.3, 126.6, 123.9, 109.1, 106.9, 78.2, 55.4, 13.9. GC–MS: 176 (70), 175 (27), 174 (13), 162 (11), 161 (100), 160 (22), 159 (11), 146 (19), 145 (30), 133 (19), 132 (10), 131 (20), 118 (13), 116 (12), 115 (35), 105 (11), 103 (24), 102 (11), 91 (12), 89 (13), 79 (12), 78 (10), 77 (34), 75 (10), 63 (20), 51 (13). HR-MS calcd. for $C_{11}H_{12}O_2$: 176.0837; found: 176.0835.

6-Methoxy-2-methyl-1-indenol 3c

mp 103–105 °C. ^1H NMR ($CDCl_3$) δ: 7.08 (d, 1H, *J* = 2.4 Hz), 7.01 (d, 1H, *J* = 8.0 Hz), 6.74 (dd, 1H, J_1 = 8.0, J_2 = 2.4 Hz), 6.27 (s, 1H), 4.81 (d, 1H, *J* = 8.9 Hz), 3.80 (s, 3H), 2.04 (broad s, 3H), 1.49 (d, 1H, *J* = 8.9 Hz). ^{13}C NMR ($CDCl_3$) δ: 158.0, 147.1, 146.1, 135.7, 126.5, 120.4, 113.1, 110.7, 79.0, 55.6, 13.7. GC–MS: 177 (10), 176 (87), 175 (18), 162 (11), 161 (100), 160 (33), 159 (18), 146 (15), 145 (40), 133 (23), 131 (12), 118 (17), 117 (16), 116 (19), 115 (60), 105 (13), 103 (20), 102 (11), 91 (13), 79 (11), 77 (24), 63 (17), 51 (16). HR-MS calcd. for $C_{11}H_{12}O_2$: 176.0837; found: 176.0841.

General method for the preparation of esters 1a–c and 2a–c

The corresponding acid chloride (4 mmol) in 5 mL of dry benzene was added to a solution of the corresponding indenol (2 mmol) and pyridine (4 mmol) in 10 mL of dry benzene. The solution was stirred overnight at room temperature, then 50 mL of water was added, and the two layers were separated. The benzene layer was washed twice with 10% aqueous HCl and once with saturated aqueous sodium bicarbonate and finally with water. The esters were purified by column chromatography on silica gel. The yields were 50–75%. Solid samples were recrystallized and oils were bulb-to-bulb distilled.

2-Methyl-1-indenyl acetate, 1a

bp 87–91 °C at 2–3 mmHg (1 mmHg = 133.322 Pa). UV (methanol) λ_{max} (nm) (ϵ ((mol $L^{-1})^{-1}$ cm^{-1})): 266 (7130), 306 (952). ^1H NMR ($CDCl_3$) δ: 7.04–7.36 (m, 4H), 6.40 (s, 1H), 6.13 (s, 1H), 2.16 (s, 3H), 1.97 (s, 3H). ^{13}C NMR ($CDCl_3$) δ: 171.4, 144.4, 143.7, 142.1, 129.3, 128.8, 125.1, 124.2, 120.3, 78.4, 21.0, 14.0. GC–MS: 188 (15), 147 (11), 146 (100), 145 (29), 131 (68), 129 (21), 128 (74), 127 (16), 117 (10), 115 (31). HR-MS calcd. for $C_{12}H_{12}O_2$: 188.0837; found: 188.0843.

5-Methoxy-2-methyl-1-indenyl acetate, 1b

UV (methanol) λ_{max} (nm) (ϵ ((mol $L^{-1})^{-1}$ cm^{-1})): 279 (2880, 306 (1560). ^1H NMR ($CDCl_3$) δ: 7.27 (d, 1H, *J* = 7.9 Hz), 6.71 (d, 1H, *J* = 2.4 Hz), 6.59 (dd, 1H, J_1 = 2.4, J_2 = 7.9 Hz), 6.38 (broad s, 1H), 6.07 (broad s, 1H), 3.79 (s, 3H), 2.17 (s, 3H), 1.98 (broad s, 3H). ^{13}C NMR ($CDCl_3$) δ: 171.6, 160.7, 145.5, 134.1, 129.1, 125, 109.4, 107.2, 78.1, 55.4, 21.1, 14.2. GC–MS: 218 (23), 177 (12), 176 (100), 175 (24), 161 (65), 160 (19), 159 (26), 158 (24), 145 (22), 144 (11), 117 (10), 116 (26), 115 (66), 91 (12). HR-MS calcd. for $C_{12}H_{14}O_3$: 218.0943; found: 218.0931.

6-Methoxy-2-methyl-1-indenyl acetate, 1c

bp 100–102 °C at 2 mmHg. UV (methanol) λ_{max} (nm) (ϵ ((mol L^{-1})$^{-1}$ cm^{-1})): 273 (8850), 320 (1190). ^{1}H NMR ($CDCl_3$) δ: 7.02 (d, 1 H, J = 8.0 Hz), 6.99 (d, 1H, J = 2.3 Hz), 6.75 (dd, 1H, J_1 = 2.3, J_2 = 8.0 Hz), 6.37 (broad s, 1H), 6.10 (broad s, 1H), 3.78 (s, 3H), 2.18 (s, 3H), 1.95 (broad s, 3H). ^{13}C NMR ($CDCl_3$) δ: 171.5, 158.1, 143.9, 142.2, 136.5, 128.9, 120.6, 114.0, 111.7, 78.5, 55.6, 21.1, 14.0. GC–MS: 218 (26), 177 (11), 176 (100), 175 (19), 161 (58), 159 (19), 158 (25), 145 (15), 116 (19), 115 (48). HR-MS calcd. for $C_{12}H_{14}O_3$: 218.0943; found: 218.0935.

2-Methyl-1-indenyl pivalate, 2a

^{1}H NMR ($CDCl_3$) δ: 7.05–7.31 (m, 4 H), 6.43 (broad s, 1H), 6.14 (broad s, 1H), 1.97 (s, 3H), 1.26 (s, 9H). ^{13}C NMR ($CDCl_3$) δ: 179.0, 144.9, 143.8, 142.4, 129.0, 128.7, 125.1, 123.9, 120.3, 78.2, 39.1, 27.3, 14.0. GC–MS: 230 (15), 146 (66), 145 (14), 131 (25), 129 (42), 128 (100), 127 (21), 115 (19), 57 (75). HR-MS calcd. for $C_{15}H_{18}O_2$: 230.1307; found: 230.1314.

5-Methoxy-2-methyl-1-indenyl pivalate, 2b

mp 63–64 °C. ^{1}H NMR ($CDCl_3$) δ: 7.21 (d, 1H, J = 8.1 Hz), 6.71 (d, 1H, J = 2.3 Hz), 6.59 (dd, 1H, J_1 = 8.1 Hz, J_2 = 2.3 Hz), 6.37 (broad s, 1H), 6.07 (broad s, 1H), 3.78 (s, 3H), 1.96 (broad s, 3H), 1.25 (s, 9H). ^{13}C NMR ($CDCl_3$) δ: 179.0, 160.6, 146.3, 145.5, 134.4, 128.8, 124.6, 109.3, 107.2, 77.8, 55.4, 39.0, 27.2, 14.1. GC–MS: 260 (11), 176 (47), 175 (21), 161 (17), 160 (11), 159 (36), 158 (29), 116 (20), 115 (40), 57 (100). HR-MS calcd. for $C_{16}H_{20}O_3$: 260.1412; found: 260.1403.

6-Methoxy-2-methyl-1-indenyl pivalate, 2c

mp 54–56 °C. ^{1}H NMR ($CDCl_3$) δ: 7.03 (d, 1H, J = 8.1 Hz), 6.92 (d, 1H, J = 2.3 Hz), 6.76 (dd, 1H, J_1 = 8.1 Hz, J_2 = 2.3 Hz), 6.37 (broad s, 1H), 6.10 (broad s, 1H), 3.78 (s, 3H), 1.94 (broad s, 3H), 1.26 (s, 9H). ^{13}C NMR ($CDCl_3$) δ: 179.0, 158.0, 144.2, 142.7, 136.5, 128.5, 120.5, 113.0, 111.6, 78.2, 55.6, 39.0, 27.2, 13.9. GC–MS: 260 (11), 176 (51), 175 (21), 161 (20), 159 (34), 158 (34), 116 (21), 115 (39), 57 (100). HR-MS calcd. for $C_{16}H_{20}O_3$: 260.1412; found: 260.1408.

Preparation of ethers, 3

The ethers were prepared from the corresponding indenols using the procedure of Freidrich and Taggart (48) and were purified by chromatography on silica gel. The yields of these reactions were not high (<20%), particularly for the methoxy-substituted cases, and the ^{1}H NMR of the crude indicated the appropriate peaks for the ethers superimposed on broad, featureless bands (oligomers?). Only one ether **9** (X = 5-OCH_3) was obtained when starting with either 5- or 6-methoxy-2-methyl-1-indenol, although GC analysis indicated that the isomer was formed (<5%). ^{1}H NOE difference spectra demonstrated that this ether was 1-methoxy-5-methoxy-2-methylindene. This ether **3** (X = 5-CH_3O) was also isolated from photolysis of 6-methoxy-2-methyl-1-indenol in methanol.

1-Methoxy-2-methylindene

^{1}H NMR ($CDCl_3$) δ: 7.02–7.42 (m, 4H), 6.42 (broad s, 1H), 4.84 (broad s, 1H), 3.02 (s, 3H), 2.02 (broad s, 3H). ^{13}C NMR ($CDCl_3$) δ: 145.9, 143.9, 141.9, 128.7, 128.4, 124.7, 123.8, 120.2, 84.9, 51.8, 14.1. GC–MS: 160 (82), 159 (11), 145 (100), 130 (14), 129 (23), 128 (45), 127 (20), 117 (40), 116 (12), 115 (60), 102 (17), 91 (22), 77 (12), 63 (18), 51 (16). HR-MS calcd. for $C_{11}H_{12}O$: 160.0888; found: 160.0887.

1-Methoxy-5-methoxy-2-methylindene

^{1}H NMR ($CDCl_3$) δ: 7.30 (d, 1H, J = 8.0 Hz), 6.72 (d, 1H, J = 2.3 Hz), 6.64 (dd, 1H, J_1 = 8.0 Hz, J_2 = 2.3 Hz), 6.39 (broad s, 1H), 4.82 (broad s, 1H), 3.81 (s, 3H), 3.02 (s, 3H), 2.03 (broad s, 3H). ^{13}C NMR ($CDCl_3$) δ: 160.3, 147.3, 145.5, 133.6, 128.4, 124.3, 109.1, 106.9, 84.2, 55.4, 52.6, 14.2. GC–MS: 191 (11), 190 (88), 189 (15), 176 (11), 175 (100), 160 (25), 159 (32), 147 (28), 144 (16), 132 (13), 116 (23), 115 (55), 103 (12), 91 (18), 89 (13), 77 (14), 63 (15), 51 (10).

Quantitative photolyses

A solution of ~100 mg of the appropriate ester **1** and **2** in 100 mL methanol or cyclohexane was purged with nitrogen and then irradiated in a Rayonet photochemical reactor using 4 lamps (75 W, 254 nm). The temperature was controlled at 25 °C by circulating water in an immersion tube. Reaction progress was monitored by GC, and the reaction stopped when the ester was less than 5% consumed. For the alcohols **3** and the ether **6** (X = H), ~50 mg in 100 mL of the appropriate solvent (methanol or cyclohexane) was used.

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