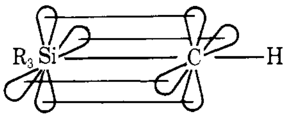
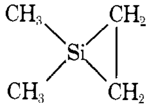


Carbene **2** is thermally stable between 4 and 40 K. To determine the behavior of **2** at higher temperatures, the matrix was warmed slowly to room temperature and the volatile product pumped away, trapped in liquid nitrogen, and subjected to GLC mass spectral analysis. Ethylene **3** was isolated and there is no evidence for formation of **4** or the intramolecular insertion product, 1,1-dimethyl-1-silacyclopropane (**11**).[13] Silyldiazomethane **1** is not altered even upon storage at >25 °C and thus **3** may be derived by capture of **2** by **1** outside of the matrix photolysis zone or/and by diazirine **5** with evolution of nitrogen.[14]

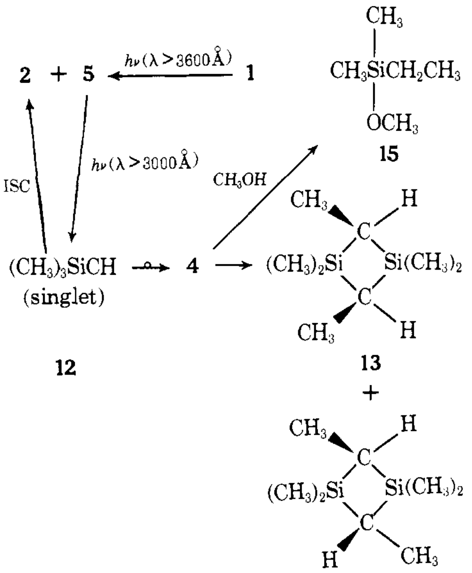


11

Photolysis of **1** or **5** at 4 °C with light of shorter wavelengths (λ >3000 Å) results in rapid destruction of the IR bands of **1** and/or **5** with formation of at least one set of new bands (Figure 3) assignable to silabutene **4**.[15,16] The infrared spectrum of the matrix product of photolysis of α-deuteriotrimethylsilyldiazomethane, presumably 3-deuterio-2-methyl-2-sila-2-butene, was determined in an attempt to assign the out-of-plane deformation for carbon–hydrogen in **4**. The weak absorption above 3000 cm^{-1} in 3-deuterio-2-methyl-2-sila-2-butene is not changed from that of **4** and therefore is not due to the carbon–hydrogen stretch. The strong band at 641 cm^{-1} in Figure 3 is shifted to 510 cm^{-1} in the spectrum of 3-deuterio-2-methyl-2-sila-2-butene and is thus assigned to the out-of-plane deformation for the lone hydrogen attached to the silicon–carbon double bond. Of significance is that the photolysis products exhibit a sharp band of medium intensity at 1377 cm^{-1} presumably for a *C*-methyl group. Such absorption is absent in **1** or **5** and is indicative of a methyl shift from silicon to carbon. The photolysis product exhibits a weak band at 1466 cm^{-1} but there is no compelling reason to assign it to the stretch of the silicon carbon double bond.[17]

To characterize silabutene **4** further, the matrix was slowly warmed to 20 °C and the volatile products were isolated. Upon comparison with authentic samples,[4b] *cis*- and *trans*-1,1,2,3,3,4-hexamethyl-1,3-disilacyclobutanes (**13** and **14**) were identified, as produced by dimerization of **4** upon destruction of the matrix. If prior to warming the matrix methanol is introduced, dimerization of **4** is suppressed and the major product is ethyldimethylmethoxysilane (**15**).

Scheme I



The present study of **1** as summarized in Scheme I illustrates the potential of solid state methods for investigating reactions of carbenes and for advantageous synthesis of highly reactive species.

Acknowledgment. We acknowledge support of this research by the Research Corporation, the National Science Foundation, The Ohio State University Graduate School, and the mass spectral contributions by R. Weisenberger.

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(9) We thank Professor O. L. Chapman, while visiting our laboratory, for pointing out that **5** is the major early product of photolysis of **1**.

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(12) R. M. Pitzer and M. R. Chedekel, unpublished results.

(13) (a) In decompositions of 1 in ref 4b, there was no evidence for **11**. Pyrolysis of **1** in cetane at 270 °C has since been found to give ethylene (~2%, and possibly dimethylsilylene) as apparently produced by collapse of **11**.[13b] At 440 °C **1** yields ethylene and 3,3,4-trimethyl-3,4-disila-1-pentene along with the products previously reported.[4b] The disilapentene is presumably formed by insertion of dimethylsilylene from **11** into dimethylvinylsilane. (b) D. Seyferth and D. C. Annarelli, *J. Am. Chem. Soc.*, **97**, 7162 (1975).

(14) Reference 1a, p 415–417.

(15) Figure 3 contains absorptions other than for **4**. Hexamethyldisiloxane is an impurity in **1** and its absorption along with that of other trace products is present in Figure 3. Detailed vibrational analysis of the spectrum of **4** is not yet feasible and comparison of present data with that calculated for silaethene[16] is not very revealing.

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Wavelength Dependent Carbonium Ion Formation by Photosolvolysis of Benzoates

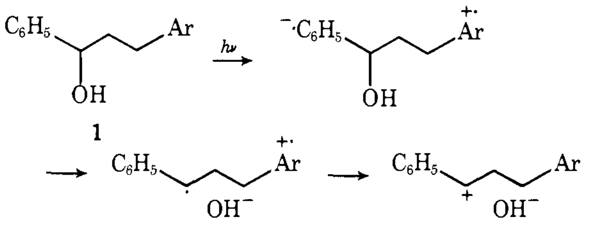
Sir:

Benzyl alcohol **1** undergoes photochemical heterolytic C–O bond cleavage by a sequence of electron transfer processes initiated by transfer from the donor *N*,*N*-dimethylaminophenyl group (eq 1).[1] We report here on studies to relocate the phenyl acceptor and the donor groups in **1** to provide a general method for photochemical formation of carbonium ions.

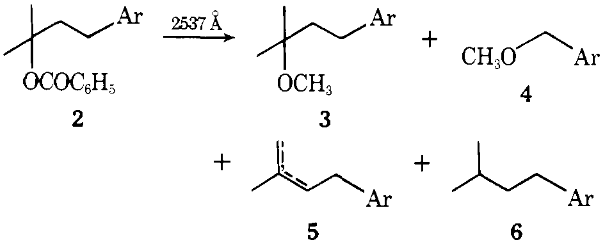
Table I. Products from 254-nm Irradiation of ~5 × 10^{-3} M Methanol Solutions of Benzoate Esters[a]

	Ester Ar = p-$C_6H_4N(CH_3)_2$	% yield nonacidic products[b]	Fraction of methyl ethers[c]
2	$C_6H_5CO_2C(CH_3)_2CH_2CH_2Ar$	85[d] (81)[d]	0.70 (0.49)
12	$C_6H_5CO_2C(CH_3)_2CH_2N(CH_3)$-$C_6H_5$	73[e] (51)[e]	0.50 (0.32)
7	m-$[Ar(CH_2)_2]C_6H_4CO_2$-$C(C_6H_{13})_3$	76[f] (68)[f]	0.24 (0.32)
8	m-$[Ar(CH_2)_3]C_6H_4CO_2$-$C(C_6H_{13})_3$	(94)[f]	(0.24)
9	$C_6H_5CO_2C(C_6H_{13})_3$	83[f] (76)[f]	0 (0.32)

[a] Values in parentheses are obtained by sensitization with ~5 × 10^{-3} M *N,N*-dimethylaniline using 300-nm light. [b] Yield of olefinic elimination products and methyl ethers based on starting material consumed. [c] Based on total nonacidic products. [d] Includes ~13% yield of **6**. [e] Includes 1,3,3-trimethylindoline, *N*-isobutyl-*N*-methylaniline and unidentified products. [f] Includes trihexylmethane.



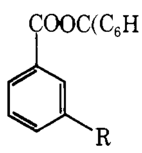
(1)



(2)

Ar = p-$C_6H_4NMe_2$

The benzoate ester **2**, in which the acceptor has been moved to the leaving group, was first selected for study since it was known that the corresponding alcohol was photochemically inert.[1] Irradiation (254 nm) of **2** in methanol yielded benzoic acid (89%) and the methyl ether **3** (52%) which, together with the fragmentation product **4** (7%), provided good evidence for intermediacy of a carbonium ion. However, unsaturated **5** and saturated **6** p-isoamylanilines that need not arise from a carbonium ion were also formed. Placement of both the donor and acceptor groups on the leaving group, **7**, similarly gave a carbonium ion-derived product, trihexylmethyl methyl ether (**10**, 18%), but the major nonacidic product (58%) was the olefinic 7-hexyl-6-tridecene (**11**).



7, R = $(CH_2)_2$-p-$C_6H_4NMe_2$
8, R = $(CH_2)_3$-p-$C_6H_4NMe_2$
9, R = H

$$\xrightarrow[R \neq H]{2537\ \text{Å}} \underset{\mathbf{10}}{CH_3OC(C_6H_{13})_3} + \underset{\mathbf{11}}{(C_5H_{11})CH{=}C(C_6H_{13})_2}$$

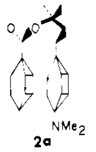
Irradiation of benzoate esters is reported to yield type II elimination products by an inefficient process that proceeds primarily through the $^1(\pi,\pi^*)$ state.[2] In order to suppress this undesired reaction **2** and **7** were photolyzed with 300-nm light which is not absorbed by the benzoate chromophore. Unexpectedly no reaction occurred; not even the methyl ethers were formed.

This observation suggested that the *N,N*-dimethylaminophenyl group might not be necessary and that carbonium ion formation might be a normal but previously overlooked side product of benzoate ester photolysis. However, irradiation (254 nm) of trihexylmethyl benzoate (**9**) in methanol gave only benzoic acid (93%) and olefin **11** (83%) with no detectable methyl ether, **10**. Moreover when **9** was labeled at the carbonyl group with ^{18}O, starting material recovered from the photolysis showed no ^{18}O scrambling. Thus the possibility that the observed reactions are unrelated to the donor group can be set aside.

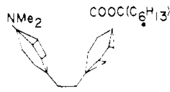
"Sensitization" by irradiation (300 nm) of *N,N*-dimethylaniline in the presence of **9** gave both the ether **10** (22%) and the olefin **11** (54%).[3] Remarkably, those compounds bearing the *N,N*-dimethylaminophenyl group, **2** and **7**, could also be "sensitized" in this manner despite the fact that internal sensitization (300 nm light) had failed. Since both the singlet (95 kcal/mol)[4] and triplet (76 kcal/mol)[5] energies of *N,N*-dimethylaniline lie below those of alkyl benzoates (E_S = 101,[4] E_T = 78 kcal/mol[2]), sensitization by an energy transfer mechanism is not likely. Nevertheless ethyl benzoate in methanol was found to quench p-*N,N*-dimethyltoluidine fluorescence (λ_{max} 354 nm, $k_q\tau$ = 60 M^{-1}), and **2**, **7**, and **8** fluoresced only extremely weakly (λ_{max} 356 nm). These observations suggest that quenching may be due to charge transfer. This is supported by the appearance of a C-T absorption band in **7** (350 nm, ϵ 910) although the other compounds studied show only the additive absorption of the separate chromophores.[6]

Piperylene quenches the reaction of 5.1 × 10^{-3} M **9** and 1.1 × 10^{-3} M *N,N*-dimethylaniline, but polymerization of the quencher together with a linear Stern–Volmer plot ($k_q\tau$ = 1100 M^{-1}) suggests that there is a single quenching process that is chemical rather than physical. Although a singlet reaction thus appears probable, the data are inadequate to rigorously exclude a triplet intermediate.

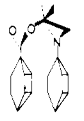
The success of the bimolecular, and failure of the intramolecular, sensitization suggests that the reaction at 300 nm might proceed through an exiplex with specific geometric requirements. Aminoester **2** can achieve only an antiparallel face-to-face complex **2a** whereas the rings in **7** must be nonparallel (**7a**). To explore other geometries we studied **8** and **12** which can attain the face-to-face crossed and parallel conformations **8a** and **12a**. Irradiation (254 nm) of **8** and **12** yielded the corresponding methyl ethers plus olefinic and radical-derived products (Table I). However, failure of any of these compounds to undergo reaction with 300-nm light appears to exclude any specific geometrical requirement.



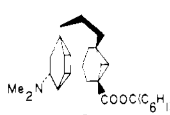
2a



7a



12a



8a

The inability to undergo intramolecular sensitization with 300-nm light suggests that solvent separated ion pairs are obligatory intermediates (eq 3–6). A charge transfer state (DA)* may be formed which dissociates to ions (eq 3) or decays by another route to the ground state (eq 4). Bond scission in (DA)* must be too slow to compete with rapid decay of this species (eq 4) but it may occur from the free ion $A\cdot^-$ (eq 5) at a rate competitive with slower diffusion controlled ion pair annihilation (eq 6).

$$(DA)^* \rightarrow D\cdot^+ + A\cdot^- \qquad (3)$$

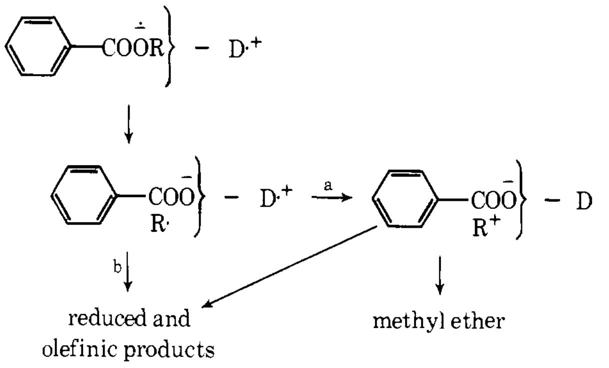
$$(DA)^* \rightarrow D + A \qquad (4)$$

$$A\cdot^- \rightarrow \text{products} \qquad (5)$$

$$D\cdot^+ + A\cdot^- \rightarrow D + A \qquad (6)$$

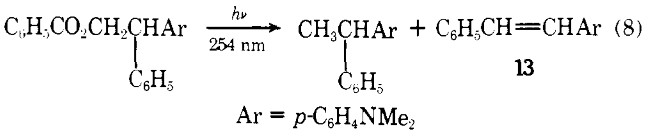
The singlet *N,N*-dimethylaminophenyl group has ample energy (88 kcal/mol)[7] to yield free ions. Thus the difference in the half wave oxidation and reduction potentials of *N,N*-dimethylaniline and methyl benzoate (+0.88 and −2.32 V, respectively) suggest that electron transfer requires only about 74 kcal/mol.[8,9] The occurrence of intramolecular sensitization with 254-nm light suggests that this may produce a higher C-T state having sufficient energy that bond scission competes effectively with decay.

The ratios of methyl ether to total nonacidic products (Table I) are consistent with the proposed mechanism (eq 7). For a given compound this ether ratio should be proportional to the fraction of products formed from carbonium ions. Unlike **7**, direct excitation of **2** and **12** yield ether ratios that are substantially higher than in the sensitized reactions. Equation 7 suggests that electron transfer (step a) should occur more rapidly upon direct excitation of **2** and **12** because the donor is attached to the incipient carbonium ion center R˙, and carbonium ion formation can thus compete more effectively with formation of radical-derived products (step b).[10]



(7)

It is of interest that when carbonium ion formation is energetically unfavorable no ether is formed (eq 8).[11]



$$C_6H_5CO_2CH_2\underset{\substack{|\\C_6H_5}}{C}HAr \xrightarrow[254\ nm]{h\nu} CH_3\underset{\substack{|\\C_6H_5}}{C}HAr + \underset{\mathbf{13}}{C_6H_5CH{=}CHAr} \qquad (8)$$

$$Ar = p\text{-}C_6H_4NMe_2$$

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Internal Reflection Resonance Raman Spectroscopy for Studies of Adsorbed Dye Layers at Electrode–Solution Interface[1]

Sir:

The in situ observation of species adsorbed at or formed in the vicinity of the electrode-solution interface during electrolysis has been one of the most exciting fields in electrochemistry and has been the subject of a number of studies in recent years.[2-4] Although a variety of methods involving internal reflection spectroscopy (IRS) using visible radiation have been developed during the course of these investigations, there have been only a few applications of Raman spectroscopy to electrochemical systems.[5-10] Fleischmann, Hendra, and McQuillan[5] were the first to demonstrate that Raman spectroscopy has a bright prospect in the study of electrode surfaces and often is a more convenient method than infrared[11,12] in such a solvent as water which gives only very weak Raman scattering. While the present work was in progress, Van Duyne and co-workers[8-10] demonstrated that vibrational spectra of electrogenerated species can be readily obtained from solutions originally ca. 1×10^{-3} M in electroactive substrate by utilizing the resonance Raman effect. Although IRS[3] has been a powerful tool for the study of electrode surfaces because of its capability of observation of the region within about one wavelength of the interface,[13,14] as yet no Raman spectra from the interface except that of a solvent[15] excited with laser beam in the internal reflection mode have been observed. In the present case the Raman spectra of adsorbed methylene blue (MB) at quartz-aqueous solution and at SnO_2 electrode-aqueous solution interfaces were obtained by utilizing the resonance Raman effect and using an Ar ion laser beam totally reflected in the optically denser solid phase side. The change in the Raman intensity as a function of electrode potential was also studied.

The Raman spectra were recorded using a Narumi double monochromater with standard photon counting detection and a CRL Ar ion laser for excitation. The resonance Raman spectra of aqueous MB solution were obtained using a rotating cell similar to that reported by Kiefer and Bernstein.[16] The cell design used for the internal reflection mode is shown in Figure 1. A quartz prism and a SnO_2 optically transparent electrode (OTE) were assembled into the cell using a silicon rubber gasket and a fluid with refractive index close to that of the optical elements. The quartz prism itself was employed as an adsorbent for the study of adsorbed MB at the quartz–aqueous solution interface. The electrical contact to the working electrode was similar to that previously described using a peripheral copper ring.[17] The auxiliary electrode was a Pt gauze and the electrode potential was referred to a saturated calomel electrode (SCE) with a Luggin capillary. The electrochemical perturbation was applied with a conventional potentiostat.

The resonance Raman spectrum of a 5×10^{-4} M aqueous MB solution excited at 514.5 nm contains the strong bands at 449, 503, 775, 861, and 1625 cm^{-1}, medium intensity bands at 957, 1073, and 1400 cm^{-1}, and weak bands at 595, 673,