

addition intermediates of type VI in the reactions of thioic esters with hydroxylic nucleophiles. The few thioacylation reactions observed (reactions 6 and 7) and the acylation and alkylation reactions of thioic esters (reactions 9 and 14) can be explained rationally as displacement reactions involving complexes such as II, V, or VII.

Experimental Section

The pulsed ICR instrumentation utilized a trapped-ion analyzer cell³³ and multiple inlet valves to admit the several gaseous neutral compounds at pressures maintained at about 10^{-6} torr. Ions were generated from the neutral molecules by electron impact at 19 eV. All reaction sequences were confirmed through double-resonance experiments and scans of ion abundance with time.

All commercially available compounds employed in this study were purified before use until chromatographically pure. *O*-methyl ethanethioate (10) and methyl ethanedithioate (12) were prepared according to published procedures from the respective imidate ester hydrochlorides, $\text{CH}_3\text{C}(\text{OCH}_3)\text{NH}_2^+\text{Cl}^-$ ³⁴ and $\text{CH}_3\text{C}(\text{SCH}_3)\text{NH}_2^+\text{Cl}^-$ ³⁵ by treatment with H_2S in pyridine.^{36,37} Deuterium-labeled esters *O*-methyl ethanethioate-*d*₃ and methyl ethanedithioate-*d*₃ were similarly prepared from the deuterium-labeled imidates $\text{CD}_3\text{C}(\text{XCH}_3)\text{NH}_2^+\text{Cl}^-$. However, ex-

tensive (40%) H-D exchange occurred on conversion of the methyl imidic ester $\text{X} = \text{S}$ to methyl ethanedithioate with H_2S in pyridine, although no exchange occurred on conversion of the methyl ester $\text{X} = \text{O}$ to *O*-methyl ethanethioate under the same conditions. It was necessary to keep the reaction time to within 5 h and the reaction temperature below -10°C in order to reduce the extent of H-D exchange in the preparation of 12-*d*₃. Even so, the maximum isotopic purity achieved in the thioacetyl methyl group was 90%, as determined by NMR and ICR analysis. Apparently, the exchange reaction occurs in the product ester rather than in the starting ester.

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Registry No. CH_3CS^+ , 59348-26-4; EtCS^+ , 87371-73-1; $\text{CH}_3\text{C}(\text{O})\text{SH}$, 507-09-5; $\text{C}_2\text{H}_5\text{C}(\text{O})\text{SH}$, 1892-31-5; $(\text{CH}_3\text{CO})_2\text{S}$, 3232-39-1; $\text{CH}_3\text{C}(\text{O})\text{SCH}_3$, 1534-08-3; $\text{CH}_3\text{C}(\text{S})\text{OCH}_3$, 21119-13-1; $\text{CD}_3\text{C}(\text{O})\text{CH}_3$, 87371-74-2; $\text{CH}_3\text{C}(\text{S})\text{SCH}_3$, 2168-84-5; $\text{CD}_3\text{C}(\text{S})\text{SCH}_3$, 81309-36-6.

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Studies on the Photochemical Reactions of α,β -Acetylenic Ketones with Tetramethylethylene

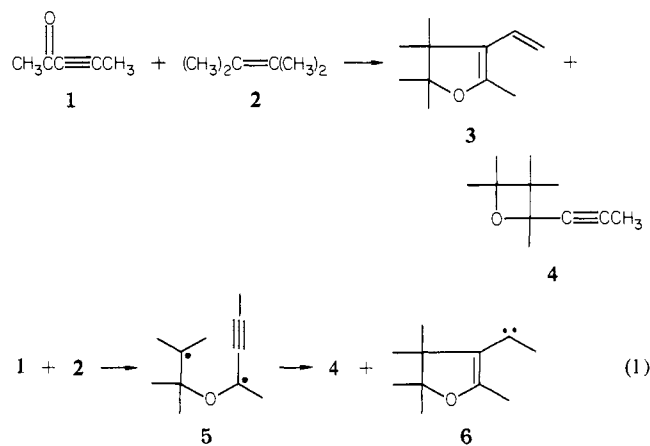
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Abstract: With exclusion of acid, photolysis of mixtures of 1 and 2 in benzene yields 7a and 8a, which rearrange readily to 3, the previously isolated product. Labeling experiments show that these dienes arise by intramolecular 1,4 transfer of hydrogen. Irradiation of 15a,b and 17 with 2 yields 21a,b and 22, respectively. These products support the intermediacy of a carbene (as 6 and 16), and irradiation in alcohols permitted capture of this intermediate as solvent adducts 25 and 26. Quenching and concentration effects on the products from 1 and 2 suggest that oxetane 4 is formed by a singlet pathway and that the [3 + 2] products come from a quenchable alkynone triplet.

In an earlier publication Hussain and Agosta briefly described the photochemical reactions of 3-pentyn-2-one (1) with tetramethylethylene (2) to yield the vinylidihydrofuran 3 and the oxetane 4.³ They recorded several related examples and noted that the simplest mechanism accounting for their results (eq 1) was formation of a biradical intermediate 5 that could collapse to the [2 + 2] product 4 or alternatively close in the [3 + 2] fashion to carbene 6, which on hydrogen migration would then yield 3. These [3 + 2] cycloadditions are novel photochemical reactions; a carbene intermediate (as 6) not only provides a credible explanation for them but also has precedent in mechanisms postulated for various other transformations of acetylenes.³ We have now investigated the reactions of 1 and several related ketones with 2 in some detail and describe below our results concerning products, the existence of the suggested carbene intermediate, and the excited states involved in these processes.

Initial Products from 1 and 2. If particular care is exercised to exclude acid from the photochemical reaction of 1 with 2 and



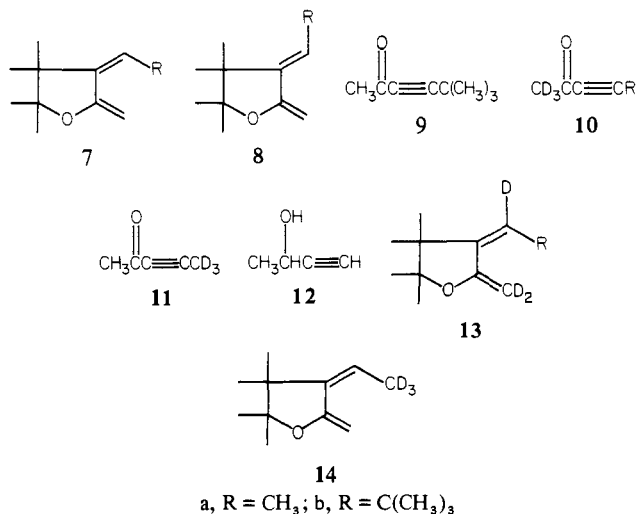
from the subsequent isolation of products, two new [3 + 2] adducts are obtained. To avoid traces of acid, solvent benzene was heated at reflux over calcium hydride and then distilled from molecular sieves before use, and a small amount of solid sodium carbonate

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or bicarbonate was added to the reaction mixture before irradiation. Under these conditions we could isolate adducts **7a** and **8a**, along with **4** and a quite small amount of **3**. These new dienes are rather unstable; a trace of acid is sufficient to effect their rapid isomerization to **3**, and this change occurs slowly without added acid in carbon tetrachloride solution at room temperature. In addition **8a** is thermally labile and isomerizes to **7a** on standing. As one might then expect, the relative amounts of **3**, **7a**, and **8a** that were obtained varied from experiment to experiment. The



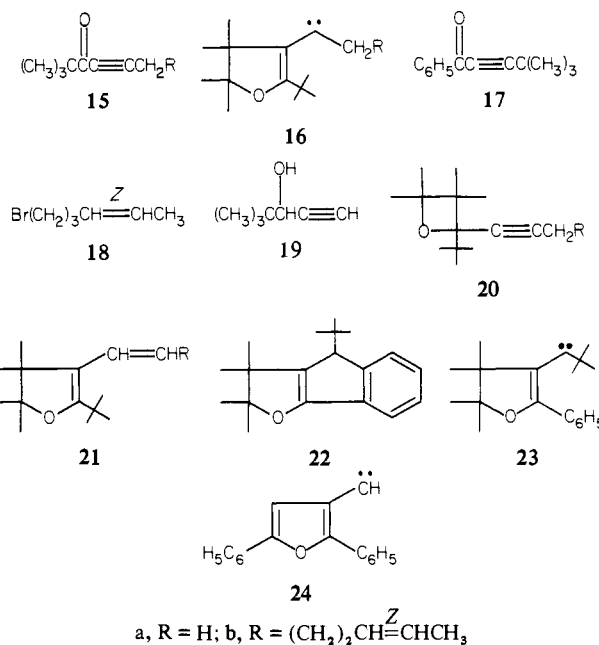
amount of **3** found was frequently so small (<2%) as to suggest that it may well not be primary product, but arise only through secondary rearrangement of **7a** and **8a**. Without precautions to eliminate acid the products isolated were **3** and **4**, as previously reported.³

The structural assignments for **7a** and **8a** are based on their interconversion and rearrangement to **3**, together with appropriate spectroscopic properties. The assignment of geometry about the double bond could be made from measurement of nuclear Overhauser effects (NOEs) in nuclear magnetic resonance (NMR) spectra of the two adducts. For one isomer transfer of energy between the vinyl methyl protons and one of the terminal methylene protons occurs in both directions in the NOE experiments, and for the other isomer similar transfer takes place between the downfield (isolated) olefinic proton and one of the terminal methylene protons, again in both directions. In both cases other expected signal enhancements also occur. These effects lead directly to assignment of the isomeric adducts as **7a** and **8a**, respectively. We note that with identification of these primary [3 + 2] adducts, it is apparent that the preferred course of rearrangement of the postulated carbene **6** is 1,4, rather than 1,2 migration of hydrogen. The assignments and properties of **7a** and **8a** parallel those reported earlier for **7b** and **8b** obtained from addition of **2** to ketone **9**.³ With **7a** and **8a** in hand, it is now clear that the effect of the *tert*-butyl group in **7b** and **8b** is simply to preclude secondary rearrangement of these primary adducts to the more stable vinylidihydrofuran system.

The Carbene Intermediate. We have carried out a number of experiments designed to provide evidence for the intermediacy of a carbene in these transformations. Photolysis of deuterium-labeled substrates **10a,b** and **11** was examined first. Ketones **10a,b** were available through repeated treatment of **1** and **9**,^{3,4} respectively, with ethanol-*O-d* and triethylamine. Ketone **11** was prepared by selective alkylation with iodomethane-*d*₃ of the dianion formed on exposure of 3-butyne-2-ol (**12**) to lithium amide⁵ and subsequent oxidation with Jones's reagent.⁶ Photocycloaddition

of these ketones to **2** yielded products having NMR spectra consistent with intramolecular 1,4-hydrogen transfer, as anticipated for a carbene intermediate. The diene from **10b** was **13b**, and the samples of **7a** from **10a** and **11** had deuterium distributed as shown in **13a** and **14**, respectively. Recovered unreacted **10a,b** and **11** had lost no deuterium; however, in **13** there had been considerable loss of label from all three olefinic positions. This loss increased on standing and could be followed easily by NMR; it was accelerated in the presence of an added trace of aqueous hydrochloric acid. Treatment of **14** with acid caused its rapid isomerization to **3** with loss of all three deuterium atoms. It seems reasonable to conclude that the incomplete labeling in the isolated samples of **13** is attributable to their sensitivity to hydrogen exchange, rather than to processes occurring during their formation.

We next examined the behavior of three other acetylenic ketones designed to reveal properties of the reactive intermediate.⁷ Two of the compounds chosen, **15a,b**, bear a *tert*-butyl adjacent to the carbonyl group, so that the postulated carbene becomes **16**, and the hydrogen transfer leading to **7** and **8** is impossible. The third



substrate is **17**, where a phenyl group adjacent to the carbonyl serves this same function. Ketone **15a** was prepared by acylation of 1-(trimethylsilyl)propyne with pivalyl chloride.⁹ For **15b**, the (*Z*)-hexenyl bromide **18** was used to alkylate⁵ acetylenic alcohol **19**,¹⁰ and the product was then oxidized.⁶ Ketone **17** was prepared as previously described.¹¹

All three compounds were irradiated with tetramethylethylene (**2**) in benzene solution under the conditions used for ketone **1**. The products from **15a** were **20a** and **21a**, demonstrating that 1,2-hydrogen transfer takes place if the preferred 1,4 shift is blocked. The long-chain ketone **15b** offered the possibility of

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(7) We also examined briefly photolysis of 1,1,1-trifluoro-3-decyn-2-one⁸ with **2**. This reaction furnished no cycloaddition products, but we did isolate in low yield a mixture of the tertiary propargylic alcohols (see i and ii in the Experimental Section) attributable to hydrogen transfer from olefin to ketone and subsequent radical coupling. It is likely that the fluorine substituents favor charge transfer and then proton transfer in this case. For a study of such effects in trifluoroacetophenone see: Wagner, P. J.; Leavitt, R. A. *J. Am. Chem. Soc.* **1973**, *95*, 3669. Wagner, P. J.; Puchalski, A. E. *Ibid.* **1978**, *100*, 5948.

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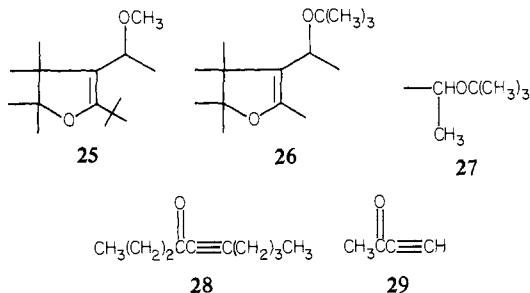
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trapping the reactive intermediate if it should behave as a radical rather than a carbene. Intramolecular addition of carbenes to distant double bonds, as might occur in **16b**, is not a favored process;¹² the corresponding radical cyclization, however, is rapid, and closure of 5-hexenyl radicals is a diagnostic method frequently employed in investigation of radical intermediates.¹³ In the event, however, photolysis of **15b** and **2** in benzene yielded oxetane **20b** and **21b**, the product of 1,2-hydrogen shift, as a 2:3 mixture of cis and trans isomers about the conjugated double bond. Vinylidihydrofurans **21a,b** were photolabile and did not accumulate well under the conditions of their formation. The phenyl ketone **17** was rapidly destroyed upon irradiation and gave a single product in 80% yield. Spectroscopic evidence indicated that this was the indenofuran **22**, understandable as the product of aromatic substitution¹⁴ by carbene **23**. This preference of **23** for intramolecular reaction stands in contrast to the behavior of 2,5-diphenyl-3-furylmethylene (**24**), which reacts intermolecularly with a variety of solvents, including benzene, rather than with the adjacent phenyl group.¹⁵ This may merely reflect the considerably lower steric hindrance about carbene **24** and its greater accessibility to solvent. Taken together these various [3 + 2] adducts originating from **1**, **15a,b**, and **17** support the intermediacy of a vinyl carbene with three reasonable, precedented modes of stabilization: 1,4-hydrogen shift;^{16,17} 1,2-hydrogen shift;¹⁶ and aromatic substitution.^{14,18}

Our strongest evidence for a carbene comes from trapping experiments that took advantage of the tendency of these intermediates to insert into O-H bonds.^{17,18} Irradiation of **15a** and **2** in methanol as solvent yielded (80%) a new product in addition to oxetane **20a** and a small amount of the vinylidihydrofuran **21a**. Analytical and spectroscopic evidence suggested that the new substance was a 1:1:1 adduct of alkynone, olefin, and methanol having structure **25**. Strong support for this assignment came



from the observation that the adduct slowly loses methanol on standing at room temperature in carbon tetrachloride solution, furnishing **21a**. A control experiment clarified the origin of **25**. Purified diene **21a** and **15a** were irradiated in solvent methanol under conditions comparable to those of the original experiment, but with no tetramethylethylene (**2**) present. Diene **21a** disappeared slowly throughout the photolysis. After 3 h no **25** was present; after 6 h a very small amount of **25** was detected by gas chromatography. In contrast, the original reaction yielded ~50% of **25** in 3 h. We conclude that the adduct is not primarily the

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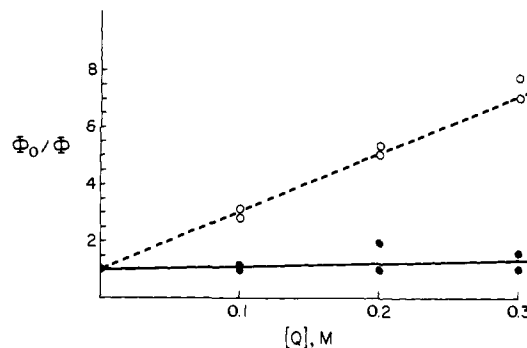


Figure 1. Stern-Volmer plot of quenching by naphthalene of reactions of **1** (0.02 M) with **2** (0.1 M): (●) formation of **4**; (○) formation of **7a**. Irradiation through 0.1 M SnCl₂ in 15% HCl ($\lambda > 305$ nm).

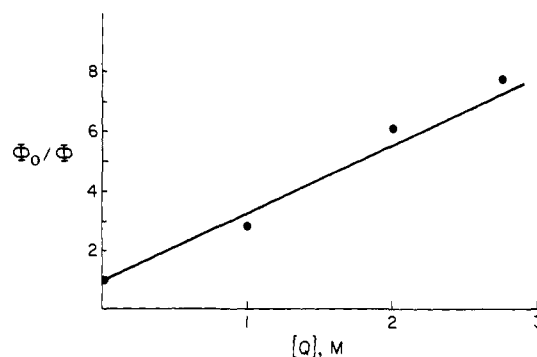


Figure 2. Stern-Volmer plot of quenching by naphthalene of disappearance of **1** (0.2 M) in reaction with **2** (1 M). Filter as for Figure 1.

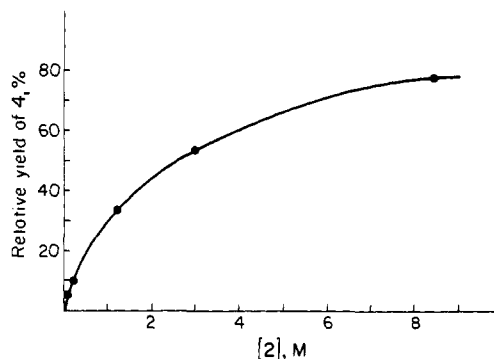


Figure 3. Relative yield of oxetane **4** with increasing concentration of **2**; [1] = 0.06 M.

product of secondary reactions between methanol and **21a** but has its origin largely in capture by methanol of an intermediate preceding **21a**. An analogous reaction occurs on photolysis of pentynone **1** and **2** in *tert*-butyl alcohol. The adduct **26** is too unstable to permit ready purification, but it could be identified through gas chromatography-mass spectrometry performed directly on the reaction mixture after irradiation. The observed spectrum included ions typical of the fragmentation of an ether with partial structure **27**.¹⁹

In sum the experiments involving deuterium labeling, the effects of structural variation in the ketone, and solvent capture of an intermediate provide strong evidence for the carbene postulated³ as an intermediate in the [3 + 2] photocycloaddition reaction.

Reactive Excited States. It was of some interest to investigate what excited states are responsible for these [2 + 2] and [3 + 2]

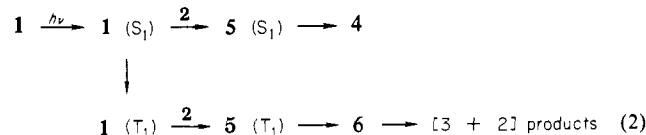
(19) These are loss of methyl, ($M - 15$)⁺, and loss of methyl and isobutylene, ($M - 71$)⁺: Budzikiewicz, H.; Djerassi, C.; Williams, D. H. "Mass Spectrometry of Organic Compounds"; Holden-Day: San Francisco, 1967; Chapter 6. Adduct **26** also has a prominent ion for loss of *tert*-butyl alcohol and methyl, ($M - 89$)⁺.

cycloaddition processes, particularly since earlier work provides little basis for an assignment. In general both singlet and triplet $n\pi^*$ states of various classes of ketones lead to oxetanes,^{20,21} and the [3 + 2] addition has no close precedents in photochemical reactions that are mechanistically well understood. Furthermore, little information is available concerning the nature or energy of the excited states of appropriate conjugated alkynones. The lowest singlet and triplet excited states of 5-decyn-4-one (**28**) in ethanol or methylcyclohexane at 77 K are reported to be $n\pi^*$ states.²² The singlet energy is given as 29 000 cm⁻¹ (82.9 kcal/mol), and from the reported maxima in the phosphorescence spectrum we estimate the triplet energy as roughly 75–77 kcal/mol. Some support for this estimate comes from our attempts to sensitize formation of **7a** and **8a** from reaction of **1** with **2**. As we discuss below, typical triplet quenchers do quench this reaction, but it was not sensitized by triplet energy transfer from acetophenone, *m*-methoxyacetophenone, or 1-indanone. Of these sensitizers, 1-indanone is reported to have the highest triplet energy, 75.6 kcal/mol.²³ Our failure to observe any sensitized reaction is then compatible with an energy of the reactive triplet of **1** of 77–78 kcal/mol or greater.

Three experiments concerning the reactive excited states in the cycloaddition of **1** with **2** are summarized in Figures 1–3. The first shows duplicate Stern–Volmer plots for the quenching of **4** and the major [3 + 2] product **7a** by naphthalene in benzene. Curves similar to that for **7a**, but less precise, result if data for the other [3 + 2] products are included or if they are plotted separately. Within experimental error there is no evidence of quenching of oxetane formation, but the [3 + 2] product is quenched efficiently. From the slope of the curve, $k_q\tau$ is 20.7 M⁻¹. In Figure 2 a Stern–Volmer plot for disappearance of **1** is given; under the conditions used ([**1**] = 0.2 M, [**2**] = 1.0 M), the unquenchable oxetane **4** is a minor product (see below), and at the naphthalene concentrations employed a linear quenching curve is obtained. This should approach a slope $k_q\tau \sim 1$ as Φ_0/Φ approaches ~ 20 . For disappearance of **1**, Φ_0 is 0.13, as determined against the Type II cleavage of valerophenone.²⁴ Figure 3 shows the variation of the amount of oxetane in the total product as a function of the concentration of **2** in the solution irradiated. As the amount of **2** is increased relative to **1**, there is a smooth increase in oxetane from less than 10% to $\sim 78\%$ of the product. The only other observed effect is a slight progressive decrease in overall rate of disappearance of **1**.

Taken together these observations suggest that interaction of **2** with a relatively short-lived, nonquenchable state of **1** yields oxetane **4**, and that, if this short-lived species is not captured by **2**, it is transformed into a longer-lived quenchable state that can add **2** with ultimate formation of the [3 + 2] products. A choice between the singlet and an unquenchable triplet state as the short-lived first species appears straightforward, since the lowest triplet of the alkynone chromophore is an $n\pi^*$ state,²² and oxetanes arise from $n\pi^*$ states of carbonyl compounds.²¹ If both [2 + 2] and [3 + 2] cycloadditions were triplet processes, the oxetane should then be formed from the lowest triplet, a requirement incompatible with the results described above. Furthermore, this lowest triplet state is ordinarily expected to be quenchable, and in fact the phosphorescence of 3-butyn-2-one (**29**) is quenched by biacetyl.²⁵ We propose then that the [2 + 2] process emanates from the first excited singlet, and that the [3 + 2] process comes from a quenchable triplet state, presumably the lowest, $n\pi^*$ triplet.²⁶

These various findings permit expansion of the mechanism previously put forward.³ The simplest scheme now in accord with our observations is shown in eq 2 for the specific case of **1** and



2. Additional complexities are not ruled out; in particular, there is considerable evidence that exciplexes play a role in related cycloadditions.²¹ Furthermore, it is worth noting that the quenching data (Figure 1) are not sufficiently precise to exclude the reasonable possibility²¹ of a minor second pathway to oxetane by way of the triplet.

Experimental Section

Materials and Equipment. Photolyses were generally performed through a uranium glass filter. All VPC was carried out by using a Varian Aerograph Model 920 gas chromatograph with one of the following columns: A, 25% Carbowax 20 M, 8 ft; B, 25% Carbowax 20 M, 6 ft; C, 25% QF 1, 3 ft; D, 25% Carbowax 20 M, 4 ft.

All columns were packed in 0.25-in. aluminum tubing with use of 45/60 Chromosorb W. Unless otherwise noted, IR and NMR spectra were obtained from solutions in CCl₄, and all pure compounds were obtained as colorless oils. The gas chromatographic–mass spectral (GC/MS) experiments were carried out on a Varian MAT CH7 instrument at 70 eV with a 2-m column of 3% SE-30 on 80/100 Suppelcoport. Other equipment has been described previously.²⁷

(*Z*)- and (*E*)-4-Ethylidene-5-methylene-2,2,3,3-tetramethyltetrahydrofuran (**7a** and **8a**). The cycloaddition between **1** and **2** was carried out as previously described,³ except that solvent benzene was heated at reflux over CaH₂ overnight and then distilled from molecular sieves before use and that solid sodium carbonate or bicarbonate (~ 3 mg/mL of solution) was added before irradiation. Products at $\sim 90\%$ conversion were isolated by VPC on column A and identified, in order of retention time, as **3**³ ($\sim 2\%$), **7a** (27%) [IR 3000–2880 (s), 1650 (m), 1385 (m), 1347 (w), 1275 (m), 1242 (m), 1125 (s), 992 (s) cm⁻¹; NMR (300 MHz, C₆D₆) δ 5.288 (q, *J* = 7.2 Hz, 1 H), 4.886 (s, 1 H), 4.35 (s, 1 H), 1.716 (d, *J* = 7.2 Hz, 3 H), 1.046 (s, 6 H), 0.835 (s, 6 H). Anal. (C₁₁H₁₈O) C, H], **4**³ (7%), and **8a** (49%) [NMR (300 MHz, C₆D₆) δ 5.840 (q, *J* = 7.5 Hz, 1 H), 4.489 (d, *J* = 1.1 Hz, 1 H), 4.391 (d, *J* = 1.1 Hz, 1 H), 1.514 (d, *J* = 7.4 Hz, 3 H), 1.049 (s, 6 H), 0.934 (s, 6 H). Anal. (C₁₁H₁₈O) C, H]. As noted in the text, **8a** isomerizes to **7a** on standing, and the amounts of **3**, **7a**, and **8a** varied from run to run.

NOE measurements were carried out at 300 MHz. Irradiation at the first given position causes enhancement at positions following: **7a**, 4.356 (4.886, 1.716), 1.716 (4.356, 5.288), 4.886 (4.356), 5.288 (1.718); **8a**, 4.391 (5.840, 4.489), 4.489 (4.391), 1.514 (5.840), 5.840 (4.391, 1.514).

Effect on Products of Concentration of **2 in Photolysis.** Benzene solutions of approximately the same total volume, 0.06 M in **1** and 0.06, 0.30, 1.2, or 3.0 M in **2**, were photolyzed as described above, along with a solution 0.06 M in **1** in **2** as solvent (8.4 M in **2**). Analysis on column B gave the results presented in Figure 3.

Preparation and Photolysis with **2 of 3-Pentyn-2-one-1,1,1-*d*₃ (**10a**).** Deuteration of **1** was carried out as for **9** below and furnished **10a** >95% deuterated in the acetyl methyl group. Photolysis of **10a** and **2** gave **13a** in which $\sim 45\%$ of the deuterium was lost from each labeled position and recovered **10a** that had retained all deuterium.

Preparation and Photolysis with **2 of 5,5-Dimethyl-3-hexyn-2-one-1,1,1-*d*₃ (**10b**).** To 250 mg of **9**^{3,4} in 1 mL of ethanol-*O-d* was added ~ 30 μ L of triethylamine. After a few hours this process was repeated and then **10b** was isolated by VPC on column B. From NMR the acetyl group of **10b** was $\sim 87\%$ deuterated. Irradiation³ of this material with **2** gave **13b** which had lost $\sim 9\%$ of its label. Over the next 24 h this sample lost (NMR) an additional 11% deuterium. Recovered **10b** had lost no deuterium.

Preparation and Photolysis with **2 of 3-Pentyn-2-one-5,5,5-*d*₃ (**11**).** By the reported procedure³ 1.0 g of 3-butyn-2-ol (**12**) was alkylated with 3.9 g of iodomethane-*d*₃ to furnish 1.1 g (97.4%) of 3-pentyn-2-ol-5,5,5-*d*₃. This was oxidized directly with Jones's reagent⁶ to yield **11** (83%) that by NMR was >95% deuterated at C(5). Photolysis of this

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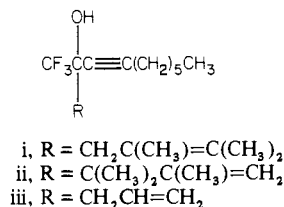
(25) Brühlmann, U.; Huber, J. R. *Helv. Chim. Acta* **1981**, 64, 2048.

(26) It is reasonable then that **17** is the only ketone investigated that furnishes no oxetane. If **17** behaves as a typical aromatic ketone, intersystem crossing is probably too fast for [2 + 2] cycloaddition to occur from the singlet.

(27) Wolff, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1983**, 105, 1292.

material with **2** yielded **14** and recovered **11**, neither of which had lost deuterium. Treatment of **14** in CCl_4 with a drop of 10% aqueous HCl quickly gave **3** with loss of all deuterium (NMR)²⁸

Photolysis of 1,1,1-Trifluoro-3-decyn-2-one with 2. A solution of 248 mg of the trifluoro ketone⁸ and 496 mg (4.9 equiv) of **2** in 20 mL of benzene was photolyzed for 44 h (~90% conversion). Analysis on column C (130 °C) gave four fractions, the largest one of which was isolated in ~8% yield. This appeared to be a ~3:1 mixture of alcohols i and ii from its spectroscopic properties and comparison with those of iii prepared below. Separation of i and ii was not successful under any VPC



conditions tried. For the mixture i and ii: IR 3621 (m), 2963 (s), 2935 (s), 2861 (m), 2221 (w), 1458 (m), 1375 (m), 1271 (m), 1175 (s), 1056 (m), 942 (w), 895 (w) cm^{-1} ; NMR (60 MHz, CDCl_3) δ 5.0 (br s), 2.61 (m), 2.42 (s, exchanges with H_2O), 2.2 (m), 2.0 (s), 1.9 (s), 1.8 (s), 1.4 (m), 0.95 (m); mass spectrum m/z 290.1837 (M^+ , calcd for $\text{C}_{16}\text{H}_{25}\text{F}_3\text{O}$, 290.1858).

Preparation of 2-(2-Propenyl)-1,1,1-trifluoro-3-decyn-2-ol (iii). Reaction of the above trifluorodecynone⁸ with allylmagnesium bromide in the usual fashion followed by purification on column C gave iii: IR 3650 (m), 3120 (w), 2940 (s), 2960 (s), 2890 (m), 2260 (w), 1640 (w), 1430 (w), 1275 (s), 1175 (s), 1120 (w), 1110 (m), 990 (w), 920 (m) cm^{-1} ; NMR (60 MHz, CDCl_3) δ 5.7 (m), 5.3 (s), 5.1 (m), 2.6 (m), 2.2 (m), 1.3 (m), 0.9 (m); mass spectrum m/z 249.1468 (M^+ , calcd for $\text{C}_{13}\text{H}_{20}\text{F}_3\text{O}$, 249.1470).

2,2-Dimethylhex-4-yn-3-one (15a). To a suspension of AlCl_3 (2.60 g, 21.6 mmol) in CH_2Cl_2 (20 mL) magnetically stirred and cooled to 0 °C was added a mixture of 1-(trimethylsilyl)propyne (2.20 g, 19.6 mmol) and pivaloyl chloride (2.875 g, 21.6 mmol) in CH_2Cl_2 (20 mL). After completion of the addition, the mixture was stirred at 15 °C for 2.5 h, washed with cold 10% HCl, H_2O , and NaHCO_3 , and dried. After removal of solvent by distillation through a Vigreux column, the residue was distilled to afford **15a** (2.198 g, 90%), bp 88–90 °C (51 mmHg); IR 2970 (s), 2215 (s), 1667 (s), 1470 (m), 1357 (w), 1267 (m), 1147 (s), 921 (s) cm^{-1} ; NMR (60 MHz) δ 2.05 (s, 3 H), 1.17 (s, 9 H). Anal. ($\text{C}_8\text{H}_{12}\text{O}$) C, H.

Photolysis of 15a. A solution of **15a** (390 mg) and **2** (1.28 g) in C_6H_6 (50 mL) was irradiated in the usual fashion until VPC analysis on column A (145 °C) indicated virtually no remaining starting material and the formation of three products. After removal of solvent by distillation, these were collected by preparative VPC. Eluted first was **21a** (~10%): IR 3115 (w), 2990 (s), 1626 (s), 1360 (s), 1319 (m), 1258 (m), 1173 (m), 1094 (s), 986 (w), 866 (m) cm^{-1} ; NMR (300 MHz) δ 6.62 (dd, $J = 11.8, 17.9$ Hz, 1 H), 4.94 (dd, $J = 1.8, 17.9$ Hz, 1 H), 4.72 (dd, $J = 1.8, 11.8$ Hz, 1 H), 1.17 (s, 9 H), 1.16 (s, 6 H), 1.05 (s, 6 H); UV λ_{max} 266 nm ($\log \epsilon = 4.09$). Anal. ($\text{C}_{14}\text{H}_{24}\text{O}$) C, H. The second component was **20a** (~5%): IR 3050 (w), 2980 (s), 2935 (m), 2225 (w), 1478 (m), 1385 (m), 1370 (m), 1125 (m), 965 (m), 938 (m) cm^{-1} ; NMR (300 MHz) δ 1.92 (s, 3 H), 1.48 (s, 3 H), 1.34 (s, 3 H), 1.27 (s, 3 H), 1.21 (s, 3 H), 1.10 (s, 9 H). Anal. ($\text{C}_{14}\text{H}_{24}\text{O}$) C, H. The third component (~5%) was unstable, partially rearranging to **21a** on standing, and was not identified.

Photolysis of **15a** (248 mg) and **2** (1.43 mL) in MeOH (40 mL) gave small amounts (<5%) of **21a** and **20a** and primarily **25** (80%): IR 2995 (s), 2830 (m), 1637 (s), 1460 (s), 1362 (s), 1070 (s) cm^{-1} ; NMR (60 MHz) δ 4.29 (q, $J = 7$ Hz, 1 H), 3.20 (s, 3 H), 1.29 (d, $J = 7$ Hz, 3 H), 1.15 (s, 9 H), 1.15–1.00 (m, 12 H); mass spectrum m/z 240 (M^+), 225, 209, 193, 109, 57. The methanol adduct is unstable in CCl_4 solution, decomposing to yield MeOH and **21a**.²⁹

No **25** was produced when pure **21a** in MeOH was photolyzed in the presence of **15a** for 3 h. After 6 h, VPC analysis indicated <10% of **25**.

Preparation of (Z)-1-Bromo-4-hexene (18). (Z)-4-Hexen-1-ol³⁰ (4.00 g, 40 mmol) in pyridine (50 mL) was treated with *p*-toluenesulfonyl chloride (10.5 g, 55 mmol) overnight at 0 °C. Standard workup yielded

the tosylate (9.43 g, 93%) which was dissolved in dimethylformamide (70 mL) and combined with NaBr (5.72 g). The mixture was stirred at 25 °C for 3 days, poured onto ice/ H_2O , and extracted with pentane. After careful removal of pentane by distillation, the residue was distilled to yield **18** (5.02 g, 83%), bp 78–9 °C (55 mmHg): IR 3020 (m), 2980 (m), 2955 (m), 1653 (w), 1428 (m), 1236 (m), 693 (m) cm^{-1} ; NMR δ 5.87–5.00 (m, 2 H), 3.37 (t, $J = 6.5$ Hz, 2 H), 2.53–1.47 [m, with d ($J = 5.5$ Hz) at 1.64, 7 H]; mass spectrum m/z 164.0023 (M^+ , calcd for $\text{C}_6\text{H}_{11}^{81}\text{Br}$, 164.0023).

Preparation of 15b. A suspension of lithium amide was prepared by adding Li (0.448 g, 64.6 mmol) to liquid NH_3 (~70 mL) and a trace of powdered $\text{Fe}(\text{NO}_3)_3$. Carbinol **19**¹⁰ (3.37 g, 30 mmol) was then added, followed by bromide **18** (5.02 g, 38 mmol). The reaction was stirred at –33 °C for 3 h and then the NH_3 was allowed to evaporate. Cold saturated NH_4Cl was added to the residue and the mixture was extracted with Et_2O (3 \times). The combined extracts were washed with H_2O and brine and dried. After removal of Et_2O , distillation afforded the desired alcohol (3.61 g, 62%), bp 82–83 °C (0.4 mmHg): IR 3655 (m), 3035 (m), 2975 (s), 2885 (m), 1358 (m), 1028 (m), 995 (m) cm^{-1} ; NMR δ 5.82–5.08 (m, 2 H), 3.95 (br s, 1 H), 2.43–1.55 (m, with d at 1.63, 10 H), 0.97 (s, 9 H). The alcohol (1.0 g) was treated with Jones's reagent in the standard fashion. Pentane workup and bulb-to-bulb distillation (115 °C, 0.5 mmHg) yielded **15b** (901 mg, 90%): IR 3030 (m), 2990 (s), 2880 (m), 2215 (s), 1668 (s), 1474 (m), 1364 (w), 1269 (w), 1145 (s), 692 (m) cm^{-1} ; NMR (300 MHz) δ 5.55–5.20 (m, 2 H), 2.38 (t, $J = 7.0$ Hz, 2 H), 2.18 (q, $J = 7.2$ Hz, 2 H), 1.68 (q, $J = 7.2$ Hz, 2 H), 1.62 (d, $J = 5.2$ Hz, 3 H), 1.17 (s, 9 H). Anal. ($\text{C}_{13}\text{H}_{20}\text{O}$) C, H.

Photolysis of 15b. Benzene solutions of **15b** with 7 equiv of **2** were irradiated in the usual fashion. From 681 mg of **15b**, 640 mg of volatile material, bp 95–205 °C (0.7 mmHg), were obtained. VPC analysis on column D (150 °C) indicated the presence of four components that were collected. The first (27%) was a mixture of the (*E*) (59%) and (*Z*) (41%) isomers of **21b**: IR 3035 (m), 3000 (s), 2880 (m), 1675 (m), 1645 (m), 1595 (m), 1477 (m), 1460 (m), 1363 (s), 1085 (s), 1025 (m), 960 (m), 868 (m), 700 (m) cm^{-1} ; NMR (300 MHz) δ 6.19 (d, $J = 16.0$ Hz, *E* isomer) and 5.76 (d, $J = 11.1$ Hz, *Z*, 1 H), 5.57–3.46 (m, 3 H), 2.11 (m, 4 H), 1.61 (m, 3 H), 1.18, 1.15, 1.14, 1.06, 0.98, 0.84 (all s, 21 H). Anal. ($\text{C}_{19}\text{H}_{32}\text{O}$) C, H. The second component (14%) was recovered **15b**. The third component (9%) was **20b**: IR 3050 (w), 3025 (m), 2980 (s), 2220 (w), 1480 (m), 1380 (m), 1366 (m), 1118 (m), 960 (m), 937 (m), 848 (m), 700 (w) cm^{-1} ; NMR (300 MHz) δ 5.52–5.28 (m, 2 H), 2.30 (t, $J = 7$ Hz, 2 H), 2.16 (q, $J = 7.2$ Hz, 2 H), 1.65–1.56 (m, 5 H), 1.50 (s, 3 H), 1.34 (s, 3 H), 1.29 (s, 3 H), 1.22 (s, 3 H), 1.11 (s, 9 H). Anal. ($\text{C}_{19}\text{H}_{32}\text{O}$) C, H. The fourth component (16%) was unstable and was not identified. On standing it decomposed yielding (*E*)-**21b** which was characterized: IR 3035 (m), 3000 (s), 2950 (s), 1641 (m), 1595 (m), 1475 (m), 1456 (m), 1361 (s), 1316 (m), 1255 (m), 1168 (m), 1091 (s), 956 (m), 865 (m), 700 (w) cm^{-1} ; NMR (300 MHz) δ 6.20 (d, $J = 16$ Hz, 1 H), 5.49–5.33 (m, 3 H), 2.12 (m, 4 H), 1.60 (d, $J = 5.3$ Hz, 3 H), 1.15 (s, 9 H), 1.14 (s, 6 H), 0.98 (s, 6 H). Anal. ($\text{C}_{19}\text{H}_{32}\text{O}$) C, H.

Photolysis of 17. A solution of **17**¹¹ (559 mg, 3 mmol) and **2** (1.515 g, 18 mmol) in C_6H_6 (50 mL) was irradiated for 2 h at which time VPC analysis on column D (190 °C) indicated the formation of one product and essentially no remaining **17**. Preparative VPC afforded pure **22** in 80% yield: IR 3090 (w), 3065 (w), 2990 (s), 2885 (m), 1663 (w), 1627 (s), 1600 (m), 1464 (s), 1398 (s), 1360 (s), 1242 (m), 1098 (s), 1066 (m), 932 (m), 713 (m) cm^{-1} ; NMR (60 MHz) δ 7.37–6.87 (m, 4 H), 3.07 (s, 1 H), 1.40 (s, 3 H), 1.28 (s, 3 H), 1.22 (s, 3 H), 1.07 (s, 3 H), 1.00 (s, 3 H). Anal. ($\text{C}_{19}\text{H}_{26}\text{O}$) C, H.

Mass Spectral Identification of 4-(1-tert-Butoxyethyl)-2,2,3,3,5-pentamethyl-2,3-dihydrofuran (26). Photolysis of **1** and **2** as above, but in *tert*-butyl alcohol as solvent, followed by GC/MS analysis indicated formation of ~30% of a solvent adduct identified as **26** on the basis of the following data:¹⁹ m/z 240 (M^+ , 7%), 225 [($\text{M} - 15$)⁺, 12%], 169 [($\text{M} - 71$)⁺, 76%], 151 [($\text{M} - 89$)⁺, 63%].

Stern-Volmer Quenching Addition of 1 to 2 by Naphthalene. Duplicate solutions of **1** (0.02 M) and **2** (0.1 M) in benzene containing naphthalene (0.0, 0.1, 0.2, and 0.3 M) were irradiated with mercury through a filter solution of 0.1 M SnCl_2 in 15% aqueous HCl ($\lambda > 305$ nm). Products **4** and **7a** were analyzed on column A with use of dodecane as internal standard. Results are presented in Figure 1. Qualitatively similar results were obtained by using 2,3-dimethyl-1,3-butadiene as quencher. In another experiment solutions of **1** (0.2 M) and **2** (1.0 M) in benzene containing naphthalene (0.0, 1.0, 2.0, 3.0 M) were irradiated as above along with a solution of valerophenone (0.2 M) in benzene as actinometer.²⁴ Hexadecane was used as internal standard. Conversion of **1** was determined by VPC and results are given in Figure 2.

Photolysis of 1 with Various Concentrations of 2. Three solutions in benzene containing **1** (0.060 M) and **2** (0.30, 1.22, 2.99 M) and one solution containing **1** (0.060 M) in **2** as solvent (8.42 M) were photolyzed

(28) We thank Dr. Saadat Hussain for first preparing **11** and investigating its photolysis.

(29) Elemental analysis of **25** was repeatedly high in carbon (~0.8%), probably due to some loss of methanol (~14%) before combustion.

(30) Bestmann, H. J.; Koschätzky, K. H.; Schätzke, W.; Süß, J.; Vostrowsky, O. *Liebigs Ann. Chem.* **1981**, 1705.

simultaneously through uranium glass for 6 h. In another experiment two solutions in benzene containing **1** (0.06 M) and **2** (0.058, 0.293 M) were similarly irradiated. Product analysis on column B gave the results shown in Figure 3.

Acknowledgment. Financial support for research in New York was provided by the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society; for research in Hamburg by Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Konrad-Adenauer-Stiftung through a fellowship to C.S.; and for both laboratories by NATO. We thank Phyllis Wilson and Eric Orava for technical assistance, S. T. Bella for microanalyses,

and Prof. David Cowburn and Mr. Francis Picart for the NOE experiment.

Registry No. **1**, 7299-55-0; **2**, 563-79-1; **4**, 80992-46-7; (*Z*)-**7a**, 87337-54-0; (*E*)-**8a**, 87337-55-1; **10a**, 87337-56-2; **10b**, 87337-58-4; **11**, 87337-60-8; **13a**, 87337-57-3; **13b**, 87337-59-5; **14**, 87337-61-9; **15a**, 71932-99-5; (*Z*)-**15b**, 87337-69-7; **17**, 17475-11-5; (*Z*)-**18**, 63281-98-1; **19**, 19115-28-7; **20a**, 87337-66-4; (*Z*)-**20b**, 87337-73-3; **21a**, 87337-65-3; (*E,Z*)-**21b**, 87337-71-1; (*Z,Z*)-**21b**, 87337-72-2; **22**, 87337-74-4; **25**, 87337-67-5; **26**, 87337-75-5; i, 87337-62-0; ii, 87337-63-1; iii, 87337-64-2; allyl bromide, 106-95-6; 1-(trimethylsilyl)propyne, 6224-91-5; pivaloyl chloride, 3282-30-2; (*Z*)-4-hexen-1-ol, 928-91-6; (*Z*)-4-hexen-1-ol tosylate, 87337-68-6; (*Z*)-2,2-dimethylundeca-9-ene-4-yne-3-ol, 87337-70-0; 1,1,1-trifluoro-3-decyn-2-one, 85336-10-3.

Photochemistry of Alkyl Halides. 10. Vinyl Halides and Vinylidene Dihalides¹

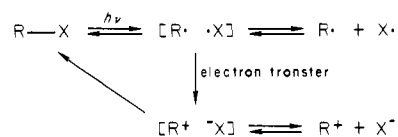
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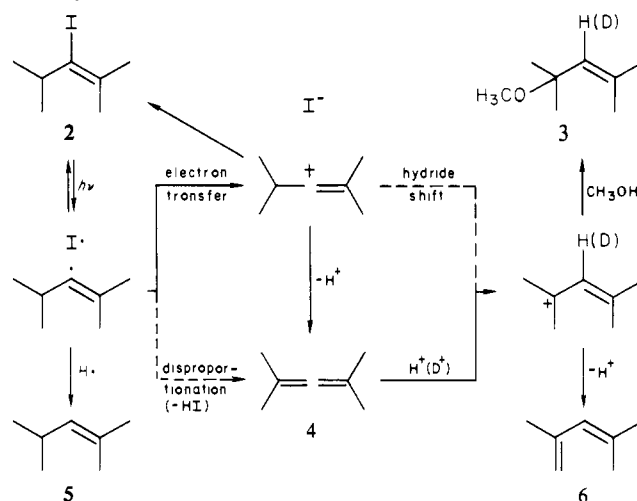
Abstract: The photobehavior of the acyclic vinyl iodide **2**, the 1-iodocycloalkenes **11–14** and **39**, the (halomethylene)cycloalkanes **45–48**, and the (dihalomethylene)cyclohexanes **62–64** has been studied. Except for the dichloride **64**, which exhibited only radical behavior, each of the halides afforded a mixture of ionic and radical products. The two bromides studied, **48** and **63**, afforded lower ratios of ionic to radical products than the corresponding iodides **45** and **62**. Irradiation of vinyl iodides was found to be a convenient and powerful method for the generation of vinyl cations, including the highly strained 1-cyclohexenyl and 1-cyclopentenyl cations and the unstabilized α -unsubstituted cations **51** and **54**. The latter cations underwent rearrangement to the ring-expanded 1-cycloalkenyl cations **28** and **36**, respectively. Lowering the temperature of the irradiation of iodides **13**, **14**, and **45** resulted in an increased ratio of ionic to radical products. However, iodide **47**, which underwent principally fragmentation to enyne **61**, showed little temperature effect.

It has long been known that absorption of light by alkyl halides generally results initially in homolytic cleavage of the carbon-halogen bond.² Recent studies in these laboratories have shown that in solution alkyl halides, particularly iodides, frequently afford photoproducts that are clearly derived from carbocationic intermediates, which we have suggested arise via electron transfer within the initially formed caged radical pair (Scheme I).^{3,4} Irradiation of alkyl halides has proven to be not only a convenient but also a powerful method for the generation of carbocationic intermediates—including such difficultly formed ions as primary carbocations and the 1-norbornyl bridgehead cation.³ We wish to report here the extension of this method to the generation of alkylvinyl cations, another class of carbocationic intermediates not easily generated by traditional ground-state methods.^{5,7}

Scheme I



Scheme II



Results

Iodide 2. The acyclic vinyl iodide **2**⁸ was prepared from ketone **1** by the general method of Pross and Sternhell.⁹ In keeping with

(1) Part 9: Kropp, P. J.; Pienta, N. J. *J. Org. Chem.* **1983**, *47*, 2084–2090.

(2) For a review of the photobehavior of alkyl halides prior to our studies, see: Sammes, J. P. "Chemistry of the Carbon-Halogen Bond"; Patai, S., Ed.; Wiley: New York, 1973; Chapter 11.

(3) Kropp, P. J.; Poindexter, G. S.; Pienta, N. J.; Hamilton, D. C. *J. Am. Chem. Soc.* **1976**, *98*, 8135–8144.

(4) A number of reports have appeared concerning the photosolvolysis of benzyl halides: (a) Zimmerman, H. E.; Sandel, V. R. *J. Am. Chem. Soc.* **1962**, *85*, 915–922. (b) Ivanov, V. B.; Ivanov, V. L.; Kuz'min, M. G. *J. Org. Chem. USSR (Engl. Transl.)* **1973**, *9*, 345–347. (c) Cristol, S. J.; Greenwald, B. E. *Tetrahedron Lett.* **1976**, 2105–2108. (d) Appleton, D. C.; Brocklehurst, B.; McKenna, J.; McKenna, J. M.; Thackeray, S.; Walley, A. R. *J. Chem. Soc., Perkin Trans. 2* **1980**, 87–90. (e) Slocum, G. H.; Kaufmann, K.; Schuster, G. B. *J. Am. Chem. Soc.* **1981**, *103*, 4625–4627. (f) Cristol, S. J.; Bindel, T. H. *Ibid.* **1981**, *103*, 7287–7293. These systems display photobehavior that differs substantially from that of alkyl analogues and, at least in part, apparently follows different mechanistic pathways.

(5) Solvolytic generation of alkylvinyl cations from vinyl precursors requires leaving groups having high nucleofugacity, such as the so-called super leaving groups CF₃SO₃ (triflate) and C₄F₉SO₃ (nonaflate); see ref 6.

(6) For a recent review of vinyl cations, see: Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. "Vinyl Cations"; Academic Press: New York, 1979.

(7) For a preliminary report of the present work, see: McNeely, S. A.; Kropp, P. J. *J. Am. Chem. Soc.* **1976**, *98*, 4319–4320.

(8) Byrd, L. R.; Caserio, M. C. *J. Org. Chem.* **1972**, *37*, 3881–3891.

(9) Pross, A.; Sternhell, S. *Aust. J. Chem.* **1970**, *23*, 989–1003. See: Barton, D. H. R.; O'Brien, R. E.; Sternhell, S. *J. Chem. Soc.* **1962**, 470–475.