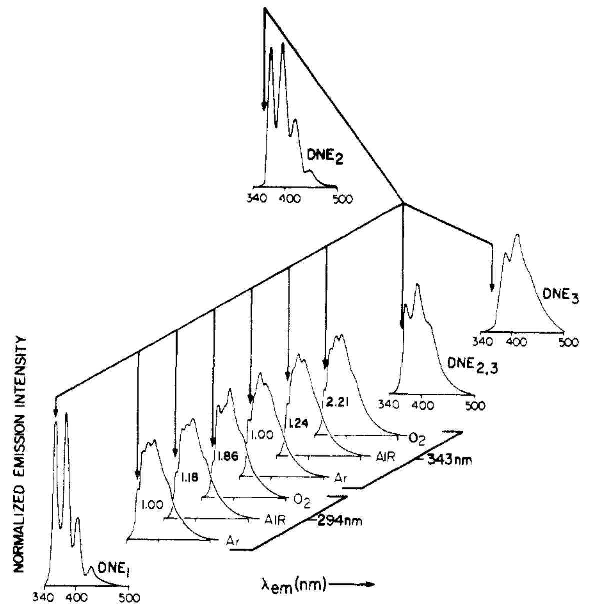

Figure 1. Typical DNE fluorescence spectra in the presence of argon, air, and O_2 at two λ_{exc}. Numbers are relative normalization factors. PCOMP component spectra are given at either end: two components for DNE alone, DNE_1 and $DNE_{2,3}$; three components for DNE, MDNE, and DMDNE together DNE_1, $DNE_2(MDNE_1)$, and $DNE_3(DMDNE)$. Arrows indicate position of λ = 360 nm for each spectrum.

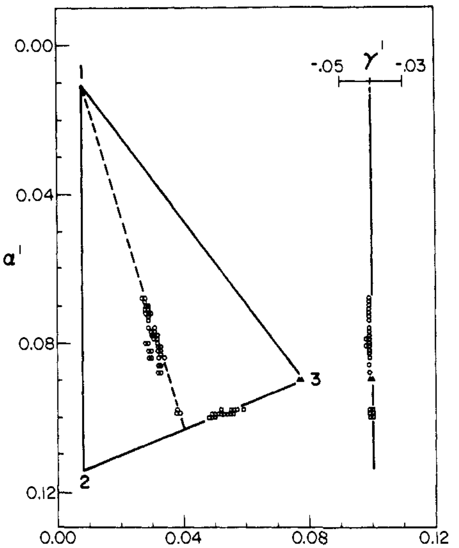

Figure 2. Orthogonal and edge views of triangle from plot of coefficients for a three-component solution, DNE (○), MDNE (□), and DMDNE (△); most points represent several independent spectra (148 total).

are two equivalent DNE_2 structures).

Stern–Volmer constants, K_{sv}, for O_2 quenching, obtained from the dependence of normalization factors and fractional contributions on $[O_2]$,[5] are given below the structures. Since, in contrast to NPE,[5] these K_{sv}'s are independent of λ_{exc}, it appears that in DNE each conformer exhibits one characteristic fluorescence lifetime.[3a,10,11] Assuming $k_q = 3.0 \times 10^{10}$ M^{-1} s^{-1} for O_2 quenching,[12] fluorescence lifetimes are 7.3 ± 1.1, 3.0 ± 0.5, ad 3.0 ± 0.5 ns for DNE_1, DNE_2, and DNE_3 and 1.7 ± 0.5, 2.2 ± 0.1, and 1.7 ± 0.1 ns for $MDNE_1$, $MDNE_2$, and DMDNE, respectively. Biexponential fits of DNE fluorescence decay curves have given 7.3 ± 0.1 and 2.2 ± 0.1 ns in methylcyclohexane at room temperature[3a] and 8.6 ± 0.7 and 1.92 ± 0.04 ns in cyclohexane at 20 °C.[10] Excitation of DNE at 373 nm, which should favor absorption by DNE_3, gives monoexponential decay with τ = 1.7 ns.[3a] It is likely, therefore, that the lifetime of DNE_3 is somewhat shorter than that of DNE_2, as was inferred from differential quenching of DNE_2/DNE_3 composite fluorescence by CCl_4.[10a] The similarity of DNE_2 and DNE_3 lifetimes is reflected in the early gated time-resolved fluorescence spectrum of DNE which shows mainly strong contributions from DNE_2 and DNE_3.[10b] Assignment of DNE_3 to the most red-shifted fluorescence spectrum conforms with observations in rigid media using nonequilibrium conformer mixtures of *t*-DNE obtained from *c*-DNE isomerization.[13] Assignments of DNE_1 and DNE_2 to the other spectra agree with those based on the quasiline fluorescence spectrum of DNE obtained at 4 K in a polycrystalline *n*-hexane matrix.[14,15]

Acknowledgment. We thank P. Tunnel for technical assistance in interfacing the fluorimeter to the microcomputer. This work was supported by NSF Grant CHE 84-00706.

Supplementary Material Available: Details of the PCOMP analyses, description of the composition of spectroexcitational matrices, and tables of eigenvectors and coefficients (20 pages). Ordering information is given on any current masthead page.

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(10) (a) Ghiggino, K. P. *J. Photochem.* **1980**, *12*, 173. (b) Matthews, A. C.; Sakurovs, R.; Ghiggino, K. P. *Ibid* **1982**, *19*, 235.

(11) Fischer, E. *J. Photochem.* **1985**, *28*, 139.

(12) Patterson, L. K.; Porter, G.; Topp, M. R. *Chem. Phys. Lett.* **1970**, *7*, 612. Gijzeman, O. L. J.; Kaufman, K.; Porter, G. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 708.

(13) Castel, N.; Fischer, E. *J. Mol. Struct.* **1985**, *127*, 159.

(14) Muszkat, K. A.; Wismontski-Knittel, T. *Chem. Phys. Lett.* **1981**, *83*, 87.

(15) Syntheses of DNE, MDNE, and DMDNE and application of PCOMP to fluorescence excitation spectra will be reported in the full paper.

Tetramethylallene and 2,4-Dimethyl-1,3-pentadiene as Hydrogen Atom Acceptors in Reactions with $HMn(CO)_5$ and $HCo(CO)_4$

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Conjugated hydrocarbons such as anthracene,[1] 1,1-diphenylethylene,[2] styrene,[3] and phenylacetylene[4] react with $HMn(CO)_5$ or $HCo(CO)_4$ through initial molecule-assisted homolysis (MAH) steps,[5] hydrogen atom transfers, giving radical-pair intermediates (eq 1). For analogous reactions of 1,3-

$$\mathrm{C{=}C{-}C{=}C + HM \rightarrow [C{=}C{-}C{-}C{-}H \cdot M] \rightarrow products;\quad M = Mn(CO)_5 \text{ or } Co(CO)_4} \quad (1)$$

dienes, the natures of the initial steps are uncertain,[6,7] while for

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(1) (a) Feder, H. M.; Halpern, J. *J. Am. Chem. Soc.* **1975**, *97*, 7186. (b) Sweany, R. L.; Halpern, J. *J. Am. Chem. Soc.* **1977**, *99*, 8335. (c) Sweany, R.; Butler, S. C.; Halpern, J. *J. Organomet. Chem.* **1981**, *213*, 487.

(2) (a) Orchin, M. In "Catalytic Transition Metal Hydrides"; Slocum, E. W., Moser, W. R., Eds.; *Ann. N.Y. Acad. Sci.* **1983**, *415*, 129. (b) Roth, J. A.; Orchin, M. *J. Organomet. Chem.* **1979**, *182*, 299. (c) Nalesnik, T. E.; Orchin, M. *J. Organomet. Chem.* **1981**, *222*, C5. (d) Nalesnik, T. E.; Freudenberger, J. H.; Orchin, M. *J. Mol. Catal.* **1982**, *16*, 43.

(3) Bockman, T. M.; Garst, J. F.; King, R. B.; Marko, L.; Ungvary, F. *J. Organomet. Chem.* **1985**, *279*, 165.

(4) Bockman, T. M.; Garst, J. F. *Abstr. Pap.—Am. Chem. Soc.* **1985**, *189th*, INOR 68.

(5) (a) Pryor, W. A. In "Organic Free Radicals"; Pryor, W. A., Ed.; American Chemical Society: Washington, DC, 1978; ACS Symp. Ser. No. 69, Chapter 3, pp 33–62. (b) Harmony, J. A. K. In "Methods in Free-Radical Chemistry"; Huyser, E. S., Ed.; Dekker: New York, 1974; Vol. 5, Chapter 2, pp 101–176.

(6) Ungvary, F.; Marko, L. *Organometallics* **1984**, *3*, 1466.

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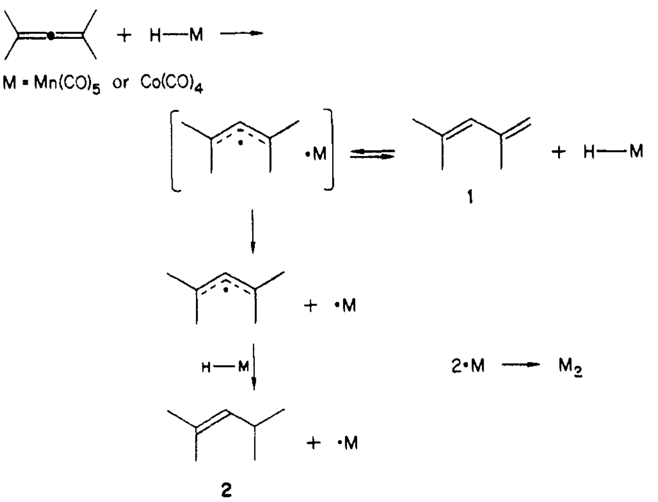
Scheme I



nonconjugated alkenes no evidence of hydrogen atom transfer has been presented. Indeed, reactions of $HCo(CO)_4$ with simple alkenes such as 1-heptene have more complex rate laws than those of hydrogen atom transfer reactions, which are simple second-order processes.[8]

Allenes are nonconjugated alkenes to which free radicals add at the central carbon (sometimes) to produce allylic radicals. However, the orthogonality of the allene π systems and the early occurrence of the transition state may prevent significant allylic delocalization and stabilization of transition states for highly exothermic radical additions.[9] MAH reactions are less exothermic. Their transition states might be later and might have geometries that are more appropriate for allylic stabilization. No data are available against which to test these conjectures; examples of allene MAH reactions are rare.[10]

These considerations lend special interest to reactions of allenes with metal hydrides. We report evidence that reactions of tetramethylallene with $HMn(CO)_5$ or $HCo(CO)_4$ proceed by initial hydrogen atom transfer (Scheme I), providing the first examples of such reactions of nonconjugated alkenes. 2,4-Dimethyl-1,3-pentadiene (**1**) also reacts with $HCo(CO)_4$, and probably $HMn(CO)_5$, through a similar mechanism (Scheme I).

In benzene at room temperature, tetramethylallene is isomerized to diene **1** and hydrogenated to 2,4-dimethyl-2-pentene (**2**) by either $HMn(CO)_5$ or $HCo(CO)_4$.[11] Diene **1** reacts more slowly than tetramethylallene with either metal hydride to give **2**.[12] The mechanism of Scheme I is supported by the second-order rate law found for reactions of tetramethylallene and diene **1** with $HMn(CO)_5$,[13] CIDNP from reactions of tetramethylallene (Figure 1) and diene **1** with $HCo(CO)_4$ and from the reaction of tetramethylallene with $HMn(CO)_5$,[14] and the similar product partitioning in reactions of excess tetramethylallene with these metal hydrides.[15]

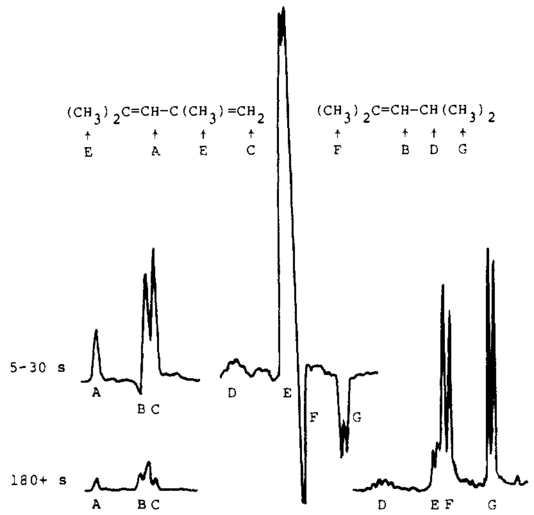


Figure 1. ^1H CIDNP in products of the reaction of tetramethylallene (0.15 M) with $HCo(CO)_4$ (0.51 M) in C_6D_6 at 29 °C. The phases conform to Scheme I and the radical pair theory of CIDNP.[20] Chemical shifts (ppm from Me_4Si): 5.60 (A), 5.00 (B), 4.85 (C), 2.45 (D), 1.75 (E), 1.50 (F), 0.95 (G).

It is unusual for geminate radical pairs of the same constitution to be formed from either of two substrates (tetramethylallene and diene **1**). This allows the reversibility of radical pair formation from tetramethylallene to be probed indirectly with isotopic experiments. While **2** from reactions of $DCo(CO)_4$ with tetramethylallene contains deuterium at C-3 (^2H NMR),[16] **2** from similar reactions of diene **1** does not. Therefore the radical pair generated from diene **1** does not produce tetramethylallene; otherwise, deuterium would appear at C-3 of **2** as a consequence of the secondary reaction of the allene with $DCo(CO)_4$. Radical pairs derived from tetramethylallene must have very nearly the same chemistry as those derived from diene **1**, since they are equivalent except for a slight difference in their initial geometries. Therefore radical-pair formation from tetramethylallene is irreversible.

Tetramethylallene is exceptionally reactive toward $HMn(CO)_5$ and $HCo(CO)_4$. For a set of similar reactions of $HMn(CO)_5$ at 29–30 °C, the relative second-order rate constants are 1.0 (tetramethylallene), 0.4 (bifluorenylidene),[2d] 0.04 (1,1-diphenylethylene),[2d] 0.02 (2,4-dimethyl-1,3-pentadiene, **1**), 0.002 (9,10-dimethylanthracene),[1c] 0.001 (α-methylstyrene),[1b] and ca. 0 (1-octene, no reaction in 5 h at 115 °C).[2c]

For tetramethylallene, $H°$ is greater than for diene **1** by an estimated 12.5 kcal/mol.[17] At least part of the high reactivity of tetramethylallene can be attributed to relief of some of this "allene strain" in the transition state for hydrogen atom transfer. It is clear, however, that energies of the transition states for hydrogen atom transfer to tetramethylallene and to diene **1** are not very similar. If they were the same, the rate constant ratio would be of order 10^8 instead of the observed order $10–10^2$. It appears that allylic delocalization and stabilization is much more highly developed in the transition state for the reaction of diene **1** than for tetramethylallene.

The finding of CIDNP from the reaction of $HCo(CO)_4$ with diene 1 contrasts with its reported absence from the similar reaction with 2,3-dimethyl-1,3-butadiene.[6] Our results indicate that concerted 1,4 addition, the mechanism proposed by Ungvary and Marko, does not describe reactions of $HCo(CO)_4$ with all conjugated dienes.[6,18] Connolly reported CIDNP from the analogous

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(7) Connolly, J. W. *Organometallics* **1984**, *3*, 1333.

(8) (a) Ungvary, F.; Marko, L. *J. Organomet. Chem.* **1981**, *219*, 397. (b) Ungvary, F. *Acta Chim. Hung.* **1982**, *111*, 117.

(9) Dewar, M. J. S.; Olivella, S. *J. Am. Chem. Soc.* **1978**, *100*, 5290.

(10) Possible example: Poutsma, M. L. *J. Org. Chem.* **1968**, *33*, 4080.

(11) Products were determined by ^1H NMR. All ^1H spectra were obtained by using a Varian EM-390 CW instrument. Proton balance [tetramethylallene + excess $HCO(CO)_4$]: 105%.

(12) With excess $HCo(CO)_4$, tetramethylallene disappears at ambient temperatures within 5 s; diene **1** persists longer.

(13) Disappearance of $HMn(CO)_5$ was monitored at 29 °C (probe temperature) by ^1H NMR. Sufficient excess tetramethylallene was used to render insignificant the secondary reaction of diene **1**. Under either CO or N_2 (1 atm), the tetramethylallene rate constant is 4×10^{-3} M^{-1} s^{-1}.

(14) Reactions at ambient temperatures of either tetramethylallene or diene **1** with $HCo(CO)_4$ give CIDNP similar to that of Figure 1. When a benzene solution of tetramethylallene and $HMn(CO)_5$ was held at 65 °C for 1 min, and then transferred to the NMR probe (29 °C) for rapid scanning, the signal at δ 0.95 was clearly emissive. No CIDNP was detected from similar reactions of diene **1**.

(15) With excess tetramethylallene, reactions of either metal hydride at 25–30 °C give ~70% **1** and ~30% **2**. Scheme I can accommodate this; the reaction and diffusion dynamics of the similar radical pairs may be similar.

(16) ^2H NMR spectra were obtained using a JEOL FX-90Q spectrometer.

(17) Estimated by the group additivity method of Benson, using tables in: Lowry, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry"; Harper and Row: New York, 1981. See also: Benson, S. W. "Thermochemical Kinetics" 2nd ed.; Wiley: New York, 1976.

reaction of $HFe(CO)_4SiCl_3$ with 1,3-cyclohexadiene but not other conjugated dienes.[7]

If the mechanism of Scheme I proves to be general for allenes, then it will be especially interesting to compare $HMn(CO)_5$–allene reactivity patterns with those for allene radical additions and 2 + 2 (biradical) cycloadditions.[19]

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(18) Several other $HCo(CO)_4$–1,3-diene reactions give CIDNP. Bockman, T. M. Ph.D. Dissertation, The University of Georgia, 1985. Ungvary, F. 1984, personal communication (isoprene).

(19) (a) Pasto, D. J. *Tetrahedron* **1983**, *40*, 2805. (b) Hopf, H. In "The Chemistry of the Allenes"; Landor, S. R., Ed.; Academic Press: New York, 1982; Vol. 2, Chapter 5, Section 5.6, pp 525–562. (c) Gajewski, J. J. "Hydrocarbon Thermal Isomerizations"; Academic Press: New York, 1981. (d) Pasto, D. J.; Yang, S.-H. *J. Am. Chem. Soc.* **1984**, *106* 152. (e) Dolbier, W. R.; Burkholder, C. R. *J. Org. Chem.* **1983**, *49*, 2381. (f) Jacobs, T. L. In "The Chemistry of the Allenes"; Landor, S. R., Ed.; Academic Press: New York, 1982; Vol. 2, Chapter 5, Section 5.3, pp 399–415. (g) Glake, P. In "The Chemistry of Ketenes, Allenes, and Related Compounds"; Patai, S., Ed.; Wiley: New York, 1980; Part 1, Chapter **9**, pp 344–347. (h) Pasto, D. J.; Warren, S. E.; Morrison, M. A. *J. Org. Chem.* **1980**, *46*, 2837. (i) Pasto, D. J.; Warren, S. E. *J. Org. Chem.* **1980**, *46*, 2842.

(20) (a) Lepley, A. R.; Closs, G. L. "Chemically Induced Magnetic Polarization"; Wiley: New York, 1973. (b) Muus, L. T.; Atkins, P. W.; McLauchlan, K. A.; Pedersen, J. B. "Chemically Induced Magnetic Polarization"; Reidel: Dordrecht, 1977.

Dewar Furan and Dewar Thiophene: Low-Temperature Matrix Photolysis of Furan and Thiophene

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Received October 15, 1985

Earlier we reported[2] the formation of Dewar thiophene (**1**) in the room-tempeature liquid-phase photolysis of thiophene (**2**), by its trapping as Diels–Alder adducts with furan (**3**). The analogous liquid-phase photolysis of furan, on the other hand, yielded furan Diels–Alder adducts with 2,3-butadienal (**4**) and cyclopropene-3-carbaldehyde (**5**) but not with Dewar furan (**6**).[3]

In an effort to gain further insight into the chemistry of these Dewar heterocycles we have examined the UV photolysis of furan and thiophene in argon matrices at 10 K and wish to report the results here.

In the IR spectrum of argon-matrix-photolyzed furan ($\lambda = 214$ nm) and thiophene ($\lambda = 229$ nm) the absorption bands due to products are few and weak: apparently a photostationary state is reached at concentrations too low to obtain satisfactory spectra of primary products. This problem was circumvented by accumulating the sequential photolysis of thin-layer deposits. The spectra obtained in these multilayer depositional sequence are far superior to the single-layer spectra. The complex IR spectra could be separated into groups of absorption bands attributable to single species on the basis of their behavior on subsequent photolysis at different wavelengths ($\lambda > 220$ nm, $\lambda = 254$ nm, $\lambda = 280$ nm, $\lambda \geq 320$ nm).

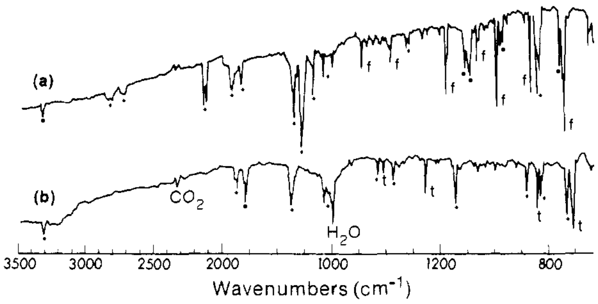
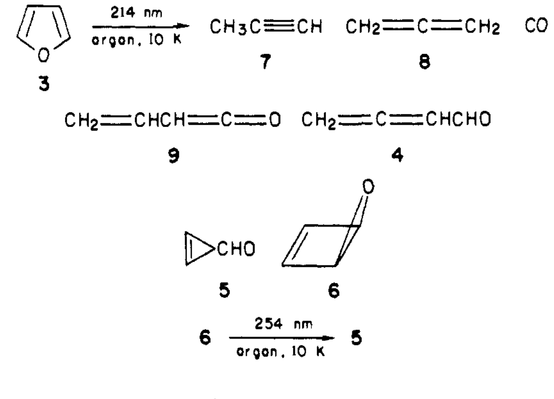


Figure 1. (a) IR spectra of $\lambda = 214$ nm multilayer photolysis of argon-matrix-isolated furan. f, furan; *, photolysis product; ●, the photolysis product is partially obscured by a background absorption. (b) IR spectrum of $\lambda = 229$ nm multilayer photolysis of argon-matrix isolated thiophene at 10 K. t, thiophene; *, photolysis product.

Scheme I



The products readily identifiable in the furan photolyzate (Figure 1a), Scheme I, were propyne (**7**), allene (**8**), and CO which were assigned by comparison with the IR spectra obtained on authentic samples under argon-matrix conditions. Vinylketene (**9**) (2137, 976, 875 cm^{-1}) was identified on the basis of comparison with the reported IR spectrum.[4] Compounds **7–9** and CO had also been observed by a Srinivasan in the gas-phase photolysis of furan,[5] indicating a correlation between the gas-phase and matrix photolysis. Also assigned were[6] 2,3-butadienal (**4**) (1965, 1925, 1665 cm^{-1}), on the basis of the prescence of allenic and carbonyl absorptions, and cyclopropene-3-carbaldehyde (**5**) (1705, 845 cm^{-1}); both of these aldehydes had been detected before as products in the liquid-phase photolysis of furan.[3] Moreover, the 400-MHz ^1H NMR spectrum of the distillate from the argon-matrix photolyzate showed two sets of absorptions on the basis of decoupling experiments at δ (CD_2Cl_2) 2.22 (1 H, d, $J = 7.7$ Hz), 7.20 (2 H, d, $J \simeq 1.2$ Hz), and 8.70 (1 H, brd, $J = 7.7$ Hz) assigned to **5**[7] and at 5.46 (2 H, d, $J = 6.0$ Hz), 5.88 (1 H, dt, $J = 7.3$, 6.0 Hz), and 9.52 (1 H, d, $J = 7.3$ Hz) assigned to **4**. The Dewar furan structure **6** has been assigned, vide infra, to the photoproduct with characteristic absorptions at 890 and 760 cm^{-1}.[8] Secondary photolysis ($\lambda = 254$ nm) clearly caused the conversion of **6** to **5**. Dewar furan also underwent photolysis conversions upon long-wavelength irradiation ($\lambda \geq 320$ nm).

Similarly in the argon-matrix photolysis ($\lambda = 229$ nm) of thiophene, Figure 1b, the formation of vinylacetylene (**10**) (3320, 890, 630 cm^{-1}), assigned by comparison with the reported spectrum,[9] and that of CS_2 and propyne (**7**) was observed. Formation of these products, Scheme II, again correlates well with the reported gas-phase photolysis of thiophene.[10]

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(1) Taken from: Rendall, W. A. Ph. D. Thesis, University of Alberta, Canada, June, 1985.

(2) Rendall, W. A.; Torres, M.; Strausz, O. P. *J. Am. Chem. Soc.* **1985**, *107*, 723–724.

(3) Rendall, W. A.; Torres, M.; Strausz, O. P. *J. Org. Chem.* **1985**, *50*, 3034–3038.

(4) Bjarnov, E. *Z. Naturforsch., A* **1979**, *34A*, 1269–1274.

(5) Srinivasan, R. *J. Am. Chem. Soc.* **1967**, *89* 1758; *Pure Appl. Chem.* **1968**, *16*, 65–74.

(6) Chapman (Chapman, O. L. *Pure Appl. Chem.* **1974**, *40*, 511–523) has briefly reported some results on the irradiation of furan in a low-temperature matrix, reporting the formation of **4** and **5**. Unfortunately we have been unable to find details of this work. Barton and Hussmann (Barton, T. J.; Hussmann, G. *J. Am. Chem. Soc.* **1983**, *105*, 6316–6318) have reported high-yield formation of allenyl aldehydes and ketones in the case of silyl-substituted furans.

(7) Previously reported (Tsuchiya, T.; Arai, H.; Igeta, H. *Tetrahedron* **1973**, *29*, 2745–2751) δ ($CDCl_3$) 2.22 (1 H, d d), 2.27 (7.27?) (2 H, d), 8.74 (1 H, d).

(8) A photoproduct with an intense absorption at 1740 cm^{-1} still remains unassigned.

(9) Popov, E. M.; Yakovlev, I. P.; Lubuzh, E. D.; Kogan, G. A. *J. Appl. Spectrosc.* **1968**, *8*, 463–468.

0002-7863/86/1508-1691$01.50/0