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

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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, $\lambda \geqslant 320$ nm).

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 ($\lambda \geqslant 320$ nm).

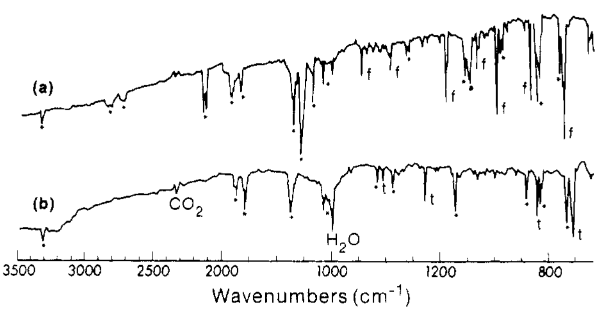
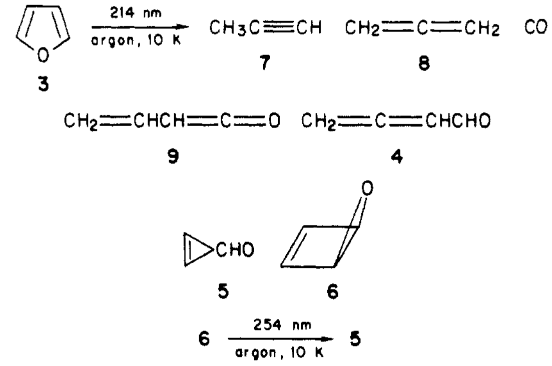


Figure 1. (a) IR spectra of $\lambda = 214$ nm multilayer photolysis of argon-matrix-isolated furan. f, furan; *, photolysis product; ●, the photolysis product is partially obscured by a background absorption. (b) IR spectrum of $\lambda = 229$ nm multilayer photolysis of argon-matrix isolated thiophene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

Scheme I



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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(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.

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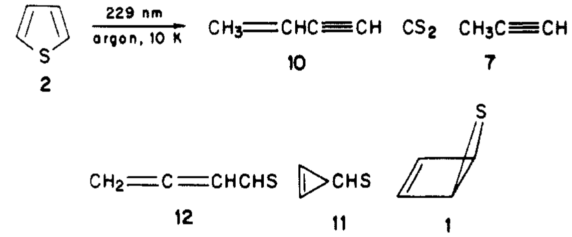
0002-7863/86/1508-1691$01.50/0

Scheme II



By analogy with the furan system the species responsible for the IR bands at 1150 and 855 cm^{-1} in the matrix photolysis of thiophene has been assigned to cyclopropene-3-thiocarbaldehyde (**11**) while the absorptions at 1950 and 1920 cm^{-1} have been assigned to 2,3-butadienthial (**12**). We have also photolyzed matrix-isolated C_4D_4 in which the 1150-cm^{-1} band remained essentially unchanged in agreement with its assignment to a thiocarbonyl absorption. The Dewar thiophene structure **1** has been assigned, vide infra, to the thiophene photoproduct responsible for the strong absorption at 740 cm^{-1}. Irradiation (254 nm) of the thiophene photolyzate caused the disappearance of the absorption bands assigned to **11** and **1** with a concomitant increase of the thiophene spectrum. Dewar thiophene also underwent photolysis at long wavelength (λ = 280 nm) and even at $\lambda > 320$ nm albeit very slowly.

In the earlier[2] solution-hase photolysis of thiophene we also trapped the Dewar isomer when thiophene was irradiated in a rigid glass at −170 °C followed by reaction with furan in the dark, thereby demonstrating that **1** was formed and intercepted under matrix conditions.

As a model for Dewar furan and Dewar thiophene, the matrix photolysis of cyclopentadiene (**13**) was investigated. van Tamelen et al.[11] reported the formation of bicyclo[2.1.0]pent-2-ene (**14**) as the sole product of UV photolysis of **13**, but no IR spectrum of **14** has been reported. Our matrix photolysis of cyclopentadiene resulted in the formation of essentially a single new product with only two strong absorptions at 720 (100%) and 770 (50%) cm^{-1} and weak absorptions (<15%) in particular at 860 and 920 cm^{-1}. This new product was subsequently distilled from the matrix and the structure determined by 400-MHz ^{1}H low-temperature NMR to be the bicyclic isomer **14**. Unexpectedly red-shifted UV absorptions have been previously reported for **14**[12] and perfluorotetramethyl Dewar thiophene.[13,14] Indeed, the photolysis (260 nm) of the argon-matrix-isolated cyclopentadiene photolyzate (and slowly with λ = 280 nm) resulted in the destruction of **14** and regeneration of **13**.

In our matrix photolysis of furan, thiophene, and cyclopentadiene we have found in each instance a strong IR absorption in the 700–800-cm^{-1} region[15] and moreover those absorptions which we have assigned to the bicyclic isomers could be selectively destroyed by irradiation at wavelength $\lambda \geq 280$ nm. Thus, we are forced to conclude that the Dewar forms of both furan and thiophene are primary products of the photolysis of **2** and **3**. Further studies are in progress.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support, R. Swindlehurst and J. Hoyle for assistance in taking the FTIR spectra, and the Alberta Heritage Scholarship Fund (WAR).

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Structures of Two Cyclopropylcarbinyl Cations[1]

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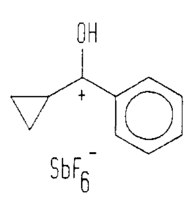
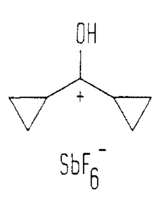
Cyclopropylcarbinyl cations have been the subject of many investigations over the past 20 years.[2] However, until now there have been no direct examinations of the structures of these cations. As stated by Sorensen:[3] "X-ray data on cyclopropylcarbinyl salts are badly needed because no experimental bond distance data is available for comparison with the calculations".

We have now prepared two substituted cyclopropylcarbinyl cations as crystalline salts and have determined their structures by single-crystal X-ray diffraction techniques. Both the hydroxycyclopropylphenylmethylium (**1**) and hydroxydicyclopropylmethylium (**2**) ions were prepared as their hexafluoroantimonate salts by protonation of the corresponding cyclopropyl ketones with HF/SbF_5. NMR spectra of solutions of these salts agree well with previously reported spectra of these ions.[4]



1



2

There are two independent cations in the asymmetric unit of **1** with very similar geometries. The structure of one of these is shown in Figure 1 and important parameters are summarized in Table I.[5] It is clear from these data that the cyclpropyl ring in **1** has adopted a conformation close to the expected "bisected" geometry. For the two molecules in each asymmetric unit, the angles made between the plane defined by the cyclopropyl carbons and the plane defined by the atoms around the formal cation center are 83.4° and 87.8°. The phenyl group, on the other hand, lies in a plane much closer to the plane around the cation center with angles between these planes of only 25.3° and 28.6°. These structures give a very beautiful demonstration of the different conformations required for effective conjugation of cyclopropyl and phenyl groups with an adjacent positive charge.

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(1) This work was supported by the Natural Sciences and Engineering Research Council of Canada.

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(5) X-ray analyses **1**: space group $P2_1/c$; unit cell, a = 13.204 (5) Å, b = 9.178 (3) Å, c = 21.369 (6) Å, β = 102.70 (3)°; 3976 unique reflections; solved using direct and difference methods; full-matrix least-squares refinement (three hydrogens were not found); final R_1 = 0.058, R_2 = 0.036. **2**: space group $P2_1/m$; unit cell, a = 7.000 (1) Å, b = 8.549 (2) Å, c = 10.849 (2) Å, β = 119.63 (1)°; 1061 unique reflections; solved using Patterson synthesis and difference methods; full-matrix least-squares refinement; final R_1 = 0.025, R_2 = 0.037. Neither of the cations appear to be perturbed by strong interactions with the counterions in the crystal lattice other than a hydrogen bonding interaction of the hydroxy proton with a fluorine in an SbF_6^- (O–H···F distances: **1**, 2.608 (5) Å, 2.787 (7) Å; **2**, 2.565 (6) Å. This type of interaction is present in all the structures of protonated ketones we have determined and of course will be present in solution. A more detailed discussion of the structure of the protonated carbonyl group will be presented in a forthcoming publication.

0002-7863/86/1508-1692$01.50/0