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do not depend on the azo group content in the copolymers, being in good agreement with the transition behavior of the backbone conformation. These results of the side-chain CD bands before and after irradiation clearly indicate that the signs of the bands are determined by the screw sense of the polypeptide chain.

In conclusion, polypeptide helix sense can be inverted by light on the basis of photoisomerization of the side-chain azobenzene moieties. This photoinduced reversible inversion in chirality might permit photocontrol in chiral recognition or chiral catalytic reactions when binding or catalytic functional groups are incorporated into the polypeptide sequence. Investigations along this line are now underway.

Absorption Spectra and Photochemical Rearrangements in Phenylalkene Cations in Solid Argon

Lester Andrews,*,† James A. Harvey,† Benuel J. Kelsall,† and Donald C. Duffey‡

Contribution from the Chemistry Departments, University of Virginia, Charlottesville, Virginia 22901, and Mississippi State University, Mississippi State, Mississippi 39762.
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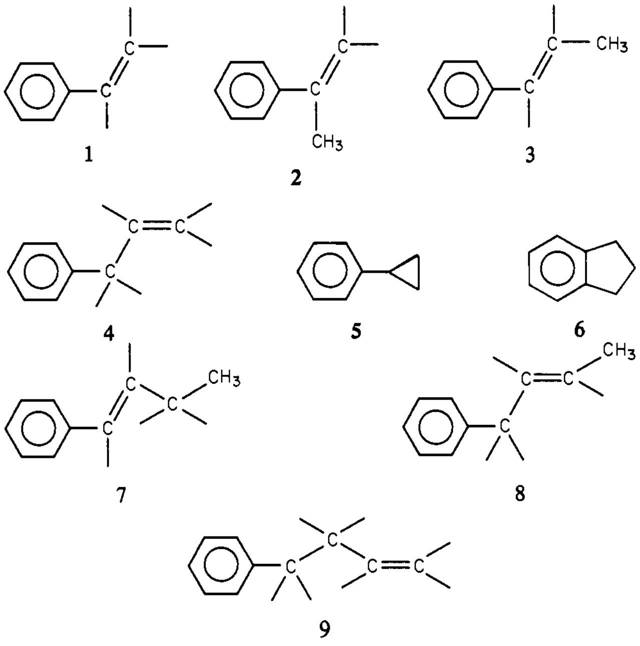
Abstract: Matrix photoionization experiments with phenylalkenes produced and trapped the parent molecular cations in solid argon at 20 K. In the substituted styrene cation cases, structure was resolved in red and ultraviolet absorption bands and assigned to Ph–C stretching and Ph—C=C bending modes. Molecular ion rearrangements were observed during sample formation and upon photolysis of the cold sample; allylbenzene cation rearranged to β-methylstyrene cation and indan cation with 290 nm irradiation. The matrix absorption bands were substantially sharper than photodissociation spectra, which suggests that excess internal energy may contribute substantially to the bandwidth of gaseous molecular ions produced by electron impact.

Styrene and substituted styrene radical cations are particularly interesting species owing to conjugation between the olefin and aromatic π systems. These ions have been produced in ion cyclotron resonance (ICR) experiments for extensive studies of photodissociation spectra (PDS).[1] The absorption spectrum of styrene cation in glassy matrices following γ-radiolysis exhibits strong bands at 630 and 342 nm.[2] The red band could not be characterized by PDS methods since this absorption energy lies below the one-photon dissociation threshold giving $C_6H_6^+$ and C_2H_2.[1]

Rearrangements of molecular ions have been of considerable interest to mass spectroscopists.[3] The PDS of allylbenzene cation was identical with that of β-methylstyrene cation showing that double-bond migration into conjugation occurs under the conditions of the ICR experiment.[1] The matrix isolation technique has recently been used to trap molecular ions for observation of absorption spectra and molecular ion rearrangements. In a particularly interesting study, cycloheptatriene cation in solid argon was rearranged to toluene cation by visible photolysis.[5] Quenching of internal energy by the matrix host makes photoisomerism a competitive process with photodissociation. Here follows a study of the absorption spectra, photochemistry, and rearrangements of phenylalkene and related cations in solid argon.

Chart I



Experimental Section

The cryogenic and vacuum apparatus and windowless argon resonance lamps have been described previously.[6,7] The experimental procedure and photolysis methods have been given in the cycloheptatriene ion report.[5] Briefly, phenylalkene vapor was diluted to about 0.5% with argon and condensed at 20 ± 2 K on a sapphire substrate with argon at 150 μm pressure flowing at about 1 mmol/h through a 3-mm i.d. orifice quartz discharge tube powered by microwave excitation. Assuming 1% photoionization of neutral molecules, an upper limit of approximately 10^{16} ions/cm^2 of sample surface may be trapped in a typical experiment. Absorption spectra were recorded on a Cary 17 spectrophotometer before and after photolysis with a high-pressure (1000 W) mercury arc, using glass wavelength cut-off filters. Photon flux from the mercury arc measured on a thermopile laser power meter arranged to match the sample configuration gave 5×10^{16} photons/(cm^2 s) in the 420–750 nm range, 8×10^{16} photons/(cm^2 s) at 290–420 nm, and 10×10^{16} photons/(cm^2 s) at 220–290 nm.

The phenylbutenes used here were obtained from ICN-K&K Laboratories, Inc.; all other samples came from Aldrich Chemical. After several freeze–thaw–pump cycles, the sample vapor was introduced di-

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† University of Virginia.
‡ Mississippi State University.

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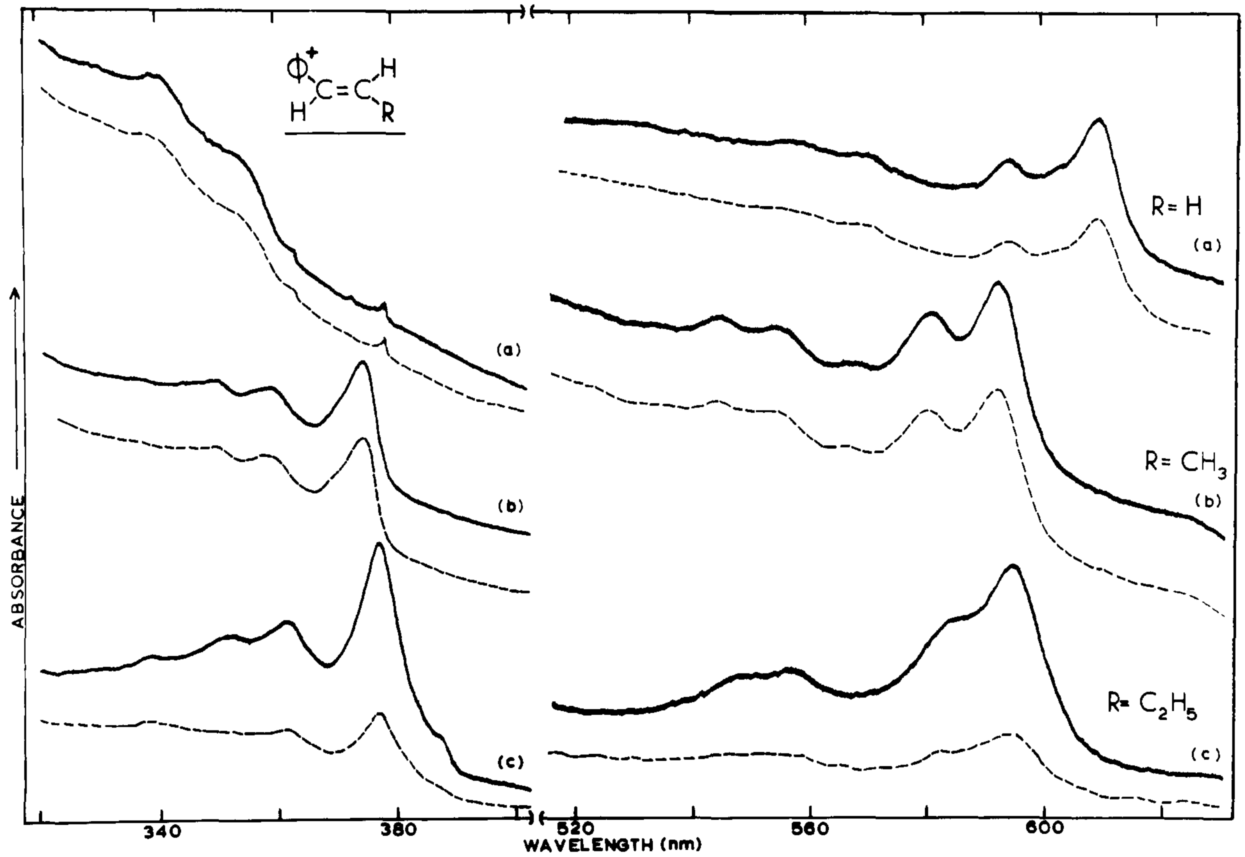

Figure 1. Absorption spectra of styrene and substituted styrenes subjected to argon resonance photoionization during condensation. (a) Styrene, UV recorded on 0.2 Å range, red on 0.1 Å range, dashed trace after 500–1000 nm photolysis. (b) β-Methylstyrene, UV recorded on 0.5 Å range, red on 0.1 Å, dashed trace after 420 nm photolysis. (c) β-Ethylstyrene, UV recorded on 0.5 Å range, red on 0.2 Å, dashed trace after 500 nm photolysis. Sample concentrations of argon/precursor were approximately 200/1.

rectly into the mixing vessel. A sample of 1-phenyl-d_5-1-propene was synthesized from C_6D_6 (Aldrich) and propionyl chloride, using standard aluminum trichloride catalyzed acylation methods. The ketone was reduced to 1-phenyl-d_5-1-propanol with $LiAlH_4$ in ether.[8] The propene was prepared by dehydrating the alcohol (3 g, 21 mmol) in 50 mL of orthophosphoric acid heated from 175 to 210 °C over 2 h;[9] the organic layer of the distillate was dried over $CaCl_2$. Matrix samples were prepared with 1-phenyl-d_5-1-propene vapor distilled from adsorption alumina.

Results

Matrix photoionization experiments with styrene, substituted styrenes, and related molecules will be described in turn.

Styrene. Eight experiments were performed with styrene (**1**), with different sample flow rates and argon pressures feeding the discharge lamp. A sample flow rate of about 2 mmol/h and a 150 mtorr argon pressure giving 1 mmol/h of argon produced the optimum yield of product species with maximum sample transmission in the ultraviolet. Higher argon pressures gave a brighter discharge and produced new signals at 373.4 nm (A = 0.10), 361.8 nm (A = 0.03), and 315.6 nm (A = 0.15), C_2^- absorptions[10] at 472.7 and 520.6 nm (A = 0.01), and only weak 608 nm absorption (A = 0.01), which indicated excessive precursor fragmentation. The spectrum shown in Figure 1a after 2 h of sample preparation with a 200/1 sample is representative of the styrene experiments. The new red absorption maximum at 608.5 (A = 0.036) is of comparable intensity with new ultraviolet bands at 353 (A = 0.032) and 339 nm (A = 0.038). These bands, and additional red peaks at 593.5, 569.0, and 566.0 nm, are listed in Table I. The 373.4, 361.8, and 315.6 nm absorptions were barely detected in the spectrum which revealed no C_2^- absorptions. These samples were subjected to photolysis with different wavelengths for 30-min periods. In two different experiments, photolysis through a Corning 2-63 glass filter (cuts off at about 560 nm, 1% transmitting at 585 nm, 70% transmitting at 608 nm) reduced both red and ultraviolet band systems by 15%. Photolysis with 500 nm cut-off radiation continued the reduction of both band systems to almost half of the original intensity, which is illustrated in the dashed trace in Figure 1a. Further 290 nm photolysis reduced both band systems to 15% of the initial intensities, destroyed the 373.4 and 361.8 nm bands, and left the 315.6 nm absorption unchanged. A similar experiment with an 800/1 sample gave slightly sharper bands with the same relative intensities.

Cyclooctatetraene (COT). Two experiments were performed with 1% COT samples in argon; one of these experiments yielded sharp, weak bands at 390.5 (A = 0.03) and 385.0 nm (A = 0.01) and the other gave no products. A final study was done on a 2% COT, 0.2% Cl_2 sample in argon. This experiment gave the 390.5 and 385.0 bands and a broad, symmetric absorption from 440 to 580 nm peaking at 500 ± 5 nm (A = 0.013). Photolysis with 450–600 nm radiation for 15 min destroyed the 505 nm absorption and produced a new broad absorption from 600 to 740 nm peaking at 650 ± 10 nm (A = 0.010). Further photolysis with 590–1000 nm light for 15 min halved the 650 nm band with no product growth elsewhere, and 290–1000 nm photolysis destroyed the broad 650 nm band and the sharp 390.5 and 385.0 nm features.

Methylstryenes. Absorption spectra for α- and β-methylstyrenes (**2** and **3**) subjected to matrix photoionization during condensation are contrasted in Figure 2. The **2** product exhibited broad peaks at 686.3 nm (A = 0.08) and 667.0 nm with a 610–630 nm wing in the red region and bands at 360.7 nm (A = 0.14) and 346.4 nm (A = 0.11) in the ultraviolet. In addition, sharper features at 317.3, 307, and 303 nm were unchanged by photolysis that destroyed the 686 and 361 nm band systems. Irradiation with 630 nm cut-off light reduced the 686 and 361 nm band systems by 10%, a like exposure to 500 nm radiation reduced both systems

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Table I. Absorption Band Positions (nm and cm^{-1}) and Vibrational Spacings (cm^{-1}) for Styrene, β-Methylstyrene, and β-Ethylstyrene Cations in Solid Argon[a]

λ, nm	ν, cm^{-1}	Δ, cm^{-1}			
		Styrene, R = H			
608.5	16 434	0	0		
593.5	16 849	415			
569.0	17 575	0	1141		
556.0	17 986	411			
339.0	29 499				
		β-Methylstyrene, R = CH_3			
591.1	16 918	0	0	0	0
579.1	17 268	350			
565.8	17 647		756		
553.8	18 057	0		1139	
543.6	18 396	339			1478
533.5	18 744	348			
373.6	26 767		0		
357.8	27 949		1182		
349.0	28 653		704		
337.2	29 656		1003		
		β-Ethylstyrene, R = C_2H_5			
594.2	16 829	0	0		
582.8	17 159	330			
556.2	17 979	0	1150		
546.3	18 305	326			
376.6	26 553		0		
361.0	27 701		1148		
350.6	28 523		822		
337.9	29 595		1072		
		β-Methylstyrene-d_5, R = CH_3			
589.4	16 966	0	0	0	0
578.4	17 289	323			
564.0	17 730		764		
553.6	18 064			1098	
547.0	18 282	0			1316
537.0	18 622	340			
372.9	26 817		0		
357.4	27 980		1163		
348.2	28 719		739		
337.0	29 674		955		

[a] Absorption band positions are accurate to better than ±10 cm^{-1} in the red and ±25 cm^{-1} in the ultraviolet.

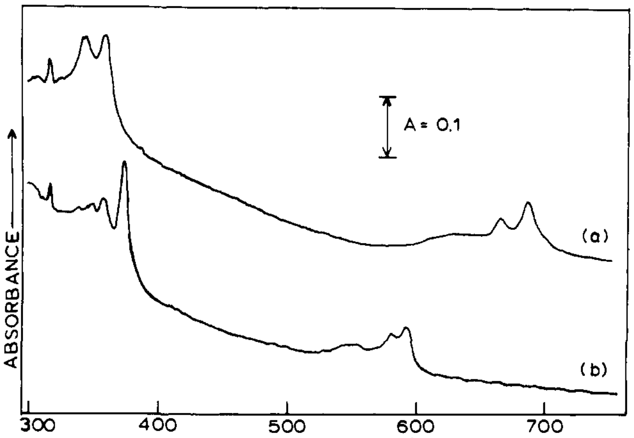

Figure 2. Absorption spectra of methyl-substituted styrenes diluted with argon to 0.5% and codeposited at 20 K with argon from an open argon discharge tube; spectra recorded on 0.5 absorbance range: (a) α-methylstyrene, (b) β-methylstyrene.

by 40%, and 290 nm photolysis destroyed both bands. Two additional experiments were performed with 2, using 1% and 0.5% H_2 in the argon passing through the discharge tube. In both cases, the yield of the photosensitive 686, 667, 361, and 346 nm bands was reduced, and the sharp 317.3 nm band intensity was markedly increased.

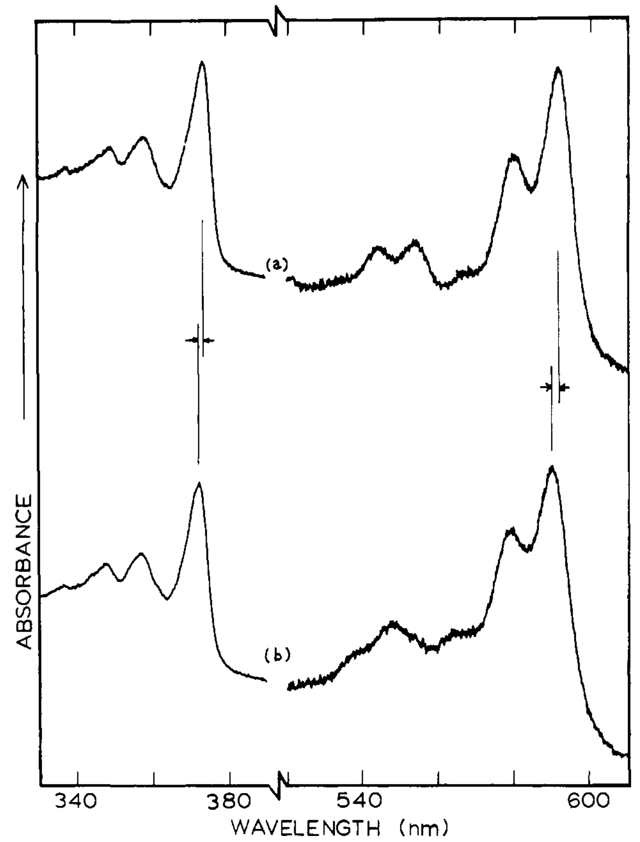

Figure 3. Absorption spectra of isotopic β-methylstyrene subjected to argon resonance photoionization during condensation; red spectra recorded on 0.1 absorbance range, UV on 0.5 range: (a) $C_6H_5CH{=}CHCH_3$, (b) $C_6D_5CH{=}CHCH_3$. Sample concentrations of argon/precursor were approximately 200/1.

Methyl substitution in the β-position had a profound affect on the product spectrum. The red and ultraviolet systems were displaced to 591.1 nm (A = 0.050) and 373.6 nm (A = 0.16) and considerable structure was resolved which is listed in Table I. The expanded scale spectrum is also illustrated in Figure 1b. Photolysis with 420 nm cut-off radiation reduced both band systems by 20%, which is shown by the dashed trace in Figure 1b. A like exposure to 290 nm light halved both bands, whereas 220 nm photolysis destroyed all but 15% of the original absorptions leaving the sharp 316.2 nm band in Figure 2b unchanged. In another experiment with 3, 585 nm irradiation for 75 min reduced both band systems by 15%, 420 nm photolysis for 60 min reduced both band systems by 40% and another 60 min exposure to this radiation continued the reduction to 50% of the initial absorbances. The spectra for *trans*-β-methyl- and β-methylstyrene samples were identical, indicating that the small amount of cis isomer in the mixture made no difference in the spectrum.

Another experiment was done with 3, using an increased (200 μm) argon inlet pressure for the discharge. The bands of interest at 591 and 373 nm were half of their intensities in the previous (150 μm) experiments. In addition, bands at 316.2, 490, and 498 nm, just detected in the previous experiments, were increased markedly, and C_2^- was observed at 520.6 nm (A = 0.046). Of particular interest, photolysis for 20 min with 515–1000 nm radiation *decreased* the sharp C_2^- band (to A = 0.037) and *decreased* the 590 (and 373) nm bands by 25% and *increased* the 490 nm band by 25%.

Four experiments were performed with the β-methylstyrene-d_5 sample; spectra for the natural isotopic and deuterated samples are compared in Figure 3 and the absorption peaks are given in Table I. Note the blue shifts in each band origin by about 50 cm^{-1} upon deuterium substitution of the aromatic hydrogens. The sharp, weak band at 315.2 nm was unchanged on the photolysis sequence that decreased the 589.4 nm (A = 0.14) and 372.9 nm (A = 0.45) band systems in concert; 30 min of 420 nm cut-off

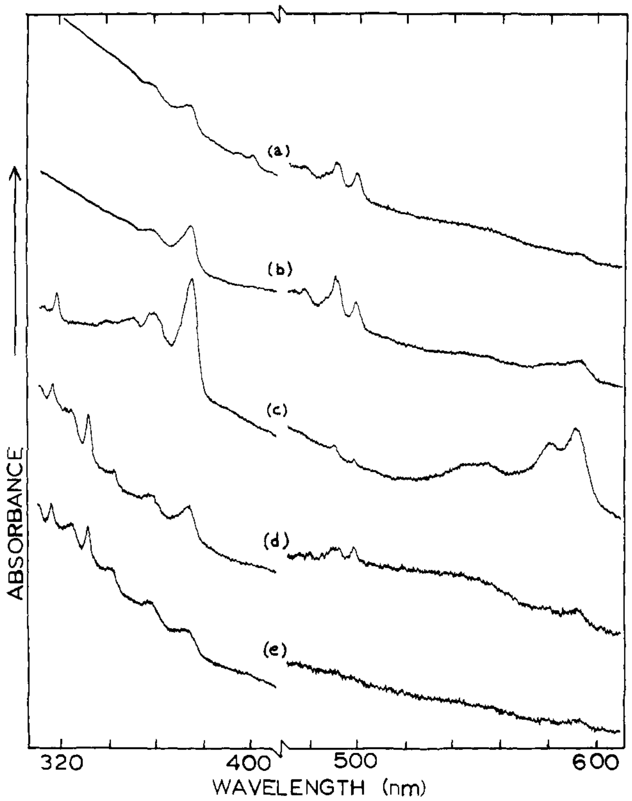

Figure 4. Absorption spectra of C_9H_{10} isomers after matrix photoionization; visible spectra recorded on 0.1 absorbance range and UV spectra recorded on 0.2 range: (a) allylbenzene, (b) sample (a) after 420–600 nm photolysis for 30 min *and* 290–1000 nm photolysis for 10 min, (c) β-methylstyrene, (d) cyclopropylbenzene, (e) sample (d) after 420–600 nm photolysis for 20 min.

radiation halved both band systems and 290 nm irradiation left about 20% of their initial absorbances.

Methyl substitution in the para position gave a spectrum similar to that of **1** in the red and **2** in the UV. The red system exhibited major peaks at 608.0 (A = 0.15) and 593.0 nm and the UV absorption revealed 361.4 (A = 0.27) and 347.0 nm (A = 0.21) maxima. Photolysis with 380–1000 nm radiation for 20 min reduced both absorption systems by 20% and a like treatment with the full arc reduced both band systems to 15% of their initial absorbances. Methyl substitution in *both* β positions of styrene gave a spectrum similar to that of **3**. The red system exhibited major absorptions at 599.0 (A = 0.08), 586.5, 561, and 550 nm and the UV system contained major peaks at 379.3 (A = 0.35) and 354 nm. Photolysis with 420–1000 nm radiation for 30 min reduced both band systems by 60%.

Allylbenzene. Two experiments with allylbenzene **4** produced a weak band at 400 nm (A = 0.007) with a 394 nm satellite, weak bands at 373 (A = 0.012) and 591 nm (A = 0.003), and a weak system at 499 (A = 0.015), 490 (A = 0.014), and 477 nm (A = 0.003), which are shown in Figure 4a. Photolysis with 420–600 nm radiation for 30 min in the first experiment caused slight increases in the 400 nm absorption and the 373 and 591 nm band systems and a decrease in the 499 nm absorption. Exposure to 290–1000 nm radiation for 10 min markedly decreased the 400 nm absorption, increased the 373 and 591 nm band systems, and increased the 499, 490, and 477 nm trio, as is illustrated in Figure 4b. Continued irradiation at 290–1000 nm for 30 more min destroyed the 400 nm absorption, decreased the 499, 490, and 477 nm trio, increased the 373 and 592 nm band systems by another 50%, and produced a weak new 426.5 absorption (A = 0.013). The 373 and 591 nm band systems are the same as those of the major product **3**, as shown by comparison with the spectrum in Figure 4c. The 499, 490, and 477 nm trio was also produced with lower yield from the **3** precursor. Photolysis with 500–1000 nm radiation for 60 min in the second experiment with **4** doubled the 490 nm absorption and reduced the 400 and 396 nm bands. Exposure to 290–1000 nm radiation for 30 min halved the 499, 490, and 477 nm bands, destroyed absorption at 400 nm, increased the 373 and 591 nm bands by 50%, and produced a new 426.5 nm band (A = 0.006). A final 220–1000 nm photolysis for 30 min reduced the 499, 490, and 477 nm bands by 75% and the 373, 591, and 426.5 nm bands by 50%.

Cyclopropylbenzene. The spectrum from the best of three cyclopropylbenzene (**5**) experiments is shown in Figure 4d. Weak bands observed at 591, 580, 373, and 358 nm are characteristic of the **3** system, and bands at 499 and 490 nm are the same as observed in the experiments using **3** and **4**. In addition, a broad band peaked at 550 nm (A = 0.007) and a new sharp band was observed at 331 nm (A = 0.048). Product features at 343 and 315.8 nm did not change during the following photolysis sequence: 420–600 nm irradiation for 20 min reduced the sharp 331 and broad 550 nm bands approximately 35%, and destroyed the 499 and 490 nm bands, as illustrated in Figure 4e, and 290–1000 nm photolysis for 20 min destroyed the 550 and 331 nm bands and left about 25% of the original product absorbances at 591 and 373 nm.

Bicyclic Precursors. One experiment was performed with indan (**6**); new product bands were observed at 475 (A = 0.006), 426.5 (A = 0.009), and 330.8 nm (A = 0.06). Photolysis with 420–1000 nm radiation reduced the 426.5 nm band (to A = 0.005) without affecting the other absorptions. A final 290–1000 nm irradiation destroyed the 426.5 nm absorption, reduced the 330.8 nm band (to A = 0.02), and left the 475 nm band unchanged. A similar experiment with tetralin (1,2,3,4-tetrahydronaphthalene) produced weak 460, 326, and 311 nm bands which exhibited no change on 420 or 290 nm photolyses.

Phenylbutenes. The spectrum of 1-phenyl-1-butene (β-ethylstyrene) (**7**) subjected to matrix photoionization resembles spectra for β-methylstyrene (**3**) and styrene (**1**), as can be seen in Figure 1; strong absorption systems were observed at 594.2 nm (A = 0.09) and 376.6 nm (A = 0.27). Additional weak bands were observed at 431 nm (A = 0.010) with a 425 nm satellite, at 453 nm (A = 0.007) with a 444 nm satellite, and at 505 nm (A = 0.005). A sharp, weak 316.0 nm band was unchanged by the following photolysis sequence: the most interesting change was a 50% *increase* in the 431 and 425 nm bands and a 15% decrease in the 594 and 376 nm band systems with 630 nm cut-off radiation without affecting the weak 453 and 505 nm bands. Further 590 and 500 nm photolysis light reduced the 594 and 376 nm systems (as shown in Figure 1c) at a greater rate than the 431 and 425 nm bands and markedly reduced the 453 and 505 nm bands. Final 290–1000 nm photolysis into all of the absorptions continued this trend.

Two experiments with the 1-phenyl-2-butene precursor (**8**) gave similar bands as the **7** sample but with different relative intensities; the 594 nm (A = 0.01) and 376 nm (A = 0.03) bands were weaker, 431, 425 (A = 0.010, 0.005), and 453 nm (A = 0.005) were similar, and stronger bands were observed at 514, 505, and 491 nm (A = 0.018, 0.038, 0.008). Photolysis with 520–1000 nm radiation for 20 min slightly decreased the 594 and 376 nm band systems and the 514 nm absorption, slightly increased the 505 nm band, and left the 431 and 435 nm feature unchanged. Photolysis with 290–1000 nm radiation for 20 min substantially reduced the 594 and 376 nm band systems and the bands at 514, 505, and 491 nm and produced a strong new 430.5 nm band (A = 0.06) with a 418 nm satellite. The latter band is identical with the toluene cation absorption produced by photolysis of cycloheptatriene cation.[5] Growth of the 430.5 nm absorption was observed upon 290 nm photolysis in three other experiments with **8**; prolonged 290 nm irradiation decreased the new band slightly and 220–1000 nm photolysis destroyed this feature.

Two experiments with 4-phenyl-1-butene (**9**) gave only weak 430, 425, and 444 nm bands, which were not changed with 500 nm photolysis, but were decreased by 290–1000 nm irradiation.

Discussion

The new product absorptions will be identified, vibrational fine structure will be assigned to substituted styrene cations, photochemical rearrangements of ions will be considered, and comparisons to gas-phase ion experiments will be made.

Styrene Cation. The absorption spectrum of styrene radical cation in *sec*-butyl chloride glass exhibited a 342 nm band and a 630 nm absorption with a 590 nm shoulder.[2] Owing to the 518 nm threshold for one-photon dissociation to $C_6H_6^+$ and C_2H_2, the PDS showed only a 330 nm peak with a 315 nm shoulder, although some presumably two-photon dissociation was observed at 579 nm.[1] The photoelectron spectrum (PES) of **1** reveals three sharp bands at 8.48, 9.28, and 10.55 eV for π ionizations before the broad σ orbital ionization onset;[11,12] the excitation energy between the first and the third sharp vertical ionizations, 2.07 ± 0.02 eV, suggests a red absorption origin at 599 ± 5 nm. The structured, photosensitive 608.5 nm band system is, therefore, assigned to styrene cation produced by argon resonance (11.6–11.8 eV) photoionization of styrene molecules during condensation with excess argon at 20 K. The 260 ± 160 cm^{-1} difference between the sharp PES band difference and the matrix absorption energy can be attributed to a matrix solvent shift. The butyl chloride matrix displaces the absorption still further to the red at 630 nm. Although the 353 and 339 nm argon matrix absorptions decreased in concert with the 608 nm band system on photolysis, the stronger 339 nm peak is intermediate between the 330 nm PDS and 342 nm glassy matrix bands for the **1** cation and this assignment is preferred. The weaker 353 nm band is probably due to another photosensitive species, possibly the styrene dimer cation.

Assignments for the optical bands of **1** cation have been given by Fu and Dunbar[1] according to an orbital energy level diagram based on ionization energies and involving interaction between the olefin and aromatic π systems. The ground state radical electron density is delocalized over both aromatic and olefin π systems with MO calculations predicting about 65% in the aromatic system.[11] On the other hand, the state reached by the red absorption has 55% of the radical electron density in the olefin π system. Accordingly, the red transition has some "charge-transfer" character. Since the upper state for the ultraviolet band has 90% of the radical electron density in the aromatic system, this transition is largely confined to the aromatic ring and is analogous to the $^2A_{2u} \leftarrow {}^2E_{1g}$ transition on benzene cation, with a blue shift owing to interaction between the olefin and ring π systems in the ground state ion. Finally, it should be noted that methyl substitution of styrene cation in the α, β, and para positions substantially increased the UV absorption band intensity relative to the red band.

In two styrene cation experiments, the sample was first photolyzed for 30 min with the intense high-pressure mercury arc through a Corning 2-63 glass filter, and both band systems were decreased by 15% in each experiment. Since this radiation is below the 518 nm one-photon threshold in the gas phase,[1] styrene ion destruction might involve a sequential two-photon dissociation process. A more likely explanation for the red photolysis behavior is neutralization by photodetachment from molecular anion electron traps in the sample, since **2** and **3** exhibited similar red photolysis behavior. Although a very weak C_2^- band[10] was detected at 520.7 nm in experiments with **1**, cold C_2^- cannot be photodetached with the radiation employed here;[13] the parent anion should, however, photodetach with red light. Photodissociation in the ultraviolet absorption bands was substantially more efficient, as shown by an 85% reduction in both styrene cation absorptions after 290–1000 nm photolysis.

Three other new absorptions were observed in experiments with **1** at 373.4, 361.8, and 315.6 nm with increased yields by using a brighter discharge lamp. The latter band was stable on photolysis, and is in agreement with a strong 315.9 nm absorption produced by mercury arc photolysis of ethyl benzene in solid argon.[14] The 315.6 nm band is assigned to the α-methylbenzyl radical, which absorbs about 5 nm higher in hydrocarbon glasses.[15] In the experiments with **1**, the $Ph\dot{C}HCH_3$ radical is formed by H atom addition to styrene, with H atoms arising from precursor photodissociation. This mechanism was confirmed by adding H_2 to the discharged argon stream in experiments with **2**, which markedly increased the yield of the dimethylbenzyl radical. Similar absorptions in α-methyl-, β-methyl-, and β-ethylstyrene experiments at 317.3, 316.2, and 316.0 are in ±0.1 nm agreement with bands produced in isopropylbenzene, *n*-propylbenzene, and *n*-butylbenzene experiments,[14] respectively, and are assigned to the $Ph\dot{C}(CH_3)_2$, $Ph\dot{C}HCH_2CH_3$, and $Ph\dot{C}CH_2CH_2CH_3$ substituted benzyl radicals. The 373.4 and 361.8 nm bands were increased at the expense of cation **1** in experiments with a higher discharge tube pressure; these bands are probably due to another fragmentation product which cannot be identified from the present data.

Table II. Comparison of Absorption Band Origins (nm) for Styrene and Methyl-Substituted Styrene Cations in Solid Argon

styrene	para	α(2)	β(3)	β,β'
608.5	608.0	686.3	591.1	599.0
339	361.4	360.7	373.6	379.3

COT Cation. The broad 500 ± 5 nm argon matrix band in COT experiments with Cl_2 added to serve as an electron trap is assigned to the COT cation, in agreement with the broad 500 nm glassy matrix[16] and 490 nm PDS observations.[1] In the radiolysis studies, $400 < \lambda < 600$ nm photolysis destroyed the broad 500 nm absorption and produced a broad 630 nm band attributed to a structured isomeric COT cation; similar results were obtained in the argon matrix. Further photolysis, $\lambda > 570$ nm, in BuCl glass reduced the 630 nm band and produced the sharp 400 nm feature, attributed to an isomeric $C_8H_8^+$ species. Owing to the photochemical isomerization of COT to benzocyclobutene,[17] the sharp 390.5 and 385.0 nm argon matrix bands are attributed to this photoisomer, tentatively identified as the benzocyclobutene cation. The PDS of COT exhibited a broad 490 nm band for the COT cation and two additional sharper 350 and 380 nm bands, which are suggested here to be contributed by the isomeric $C_8H_8^+$ benzocyclobutene cation.

Methylstyrene Cations. The photosensitive absorption bands at 591.1 and 373.6 nm in the experiments with **3** are intermediate between strong 579 and 354 nm PDS bands and 598 and 375 nm glassy matrix absorptions due to the β-methylstyrene radical cation.[1,2] The argon matrix solvent red shifts the PDS transitions by approximately 340 and 1460 cm^{-1}, respectively. The **3** cation is photosensitive, probably undergoing H atom detachment, as observed in the PDS;[1] however, owing to quenching of internal energy by the argon matrix, the **3** cation is not completely destroyed by photolysis. The β-methylstyrene-d_5 cation was prepared, and the blue deuterium shifts of the major peaks to 589.4 and 372.9 nm and 48 and 50 cm^{-1}, respectively, are supportive of this identification.

Photoelectron spectra predict a decrease in the red absorption energy for the α-methylstyrene cation as compared to styrene or β-methylstyrene cations,[12,18] which is substantiated by the spectra in Figure 2 showing the strong red absorption origin at 686 nm for the α-methylstyrene cation in contrast to 591 nm for the β-methyl derivative. This can be rationalized by an increase in the dihedral angle between the aromatic and olefin moieties for the α-methyl-substituted cation, owing to steric effects of the α-methyl group, which results in a concomitant decrease in the π interaction and the transition energy. Photoelectron spectra also predict an increase in the red transition energy for the β-methylstyrene cation as compared to the styrene cation,[1] which is confirmed by the spectra in Figure 1. Absorption band positions

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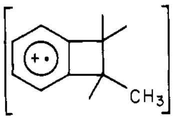
for methyl-substituted styrene cations are collected in Table II. The spacing between the two strongest peaks in the red band system, which increased from 350 cm^{-1} for the β-cation to 416 cm^{-1} for the α-cation, will be assigned below to a Ph—C=C bending vibration.

Allylbenzene Cation. The matrix photoionization of **4** produced weak bands at 591 and 373 nm which were observed in greater yield with the **3** precursor and assigned above to the **3** cation, formed here by rearrangement of the **4** cation. The photosensitive 400 nm absorption with a 394 nm shoulder is in very good agreement with the 3.3 eV energy difference between the onset of ionization and the 11.9 eV maximum in the PES of **4**.[11] This is the region expected for the $\pi \rightarrow \pi$ transition of an aromatic cation; the toluene cation absorbs, for example, at 430 nm in solid argon.[5] Accordingly, the 400 nm argon matrix absorption is assigned to the **4** cation, which is supported by the photochemical rearrangements shown in Figure 4.

New bands at 477, 490, and 499 nm in experiments with **4** were also found in experiments with **3** and **5**. These bands exhibited photolytic interconversion consistent with a structural isomer of **3** and **4** cations. An increase in the argon discharge lamp intensity favored the former product trio in experiments with **3**, suggesting either a fragment identification or the involvement of an excited species in the formation of this absorber. The observation of the indan cation upon photolysis in experiments with **4**, to be discussed below, shows that ring closure occurs in these experiments and suggests that the analogous four-membered ring benzocyclobutane cation **10** could be responsible for the 477, 490, and 499 nm absorptions. Unfortunately, this tentative identification could not be confirmed by performing an experiment with the neutral precursor, as was done for indan. The 426.5 nm band produced by photolysis in experiments with **4** is identical to a 426.5 nm photosensitive band in an experiment with indan. Assignment of this absorption to the **6** cation is in accord with the photoelectron spectrum of indan.[12]



10

Cyclopropylbenzene Cation. Matrix experiments with **5** produced photosensitive bands identified above as the **3** cation and suggested to be the **10** cation. In addition, sharp 331 nm and broad 550 nm product bands were decreased in concert on photolysis. Agreement with 310 and 539 nm PDS bands for the **5** cation indicates a like assignment for the 331 and 550 nm argon matrix absorptions.

Phenylbutene Cations. Matrix photoionization studies with **7** produced similar spectra to the **3** precursor (Figure 1). The photosensitive bands at 594.2 and 376.6 nm are assigned to the **7** cation. The 431 nm absorption and 425 nm satellite were observed in both **7** and **8** experiments; this band is in excellent agreement with the 413 nm PDS band of the **8** cation which supports this identification. The **8** precursor gave weak **7** cation bands, and in addition, stronger bands at 491, 505, and 514 nm. The position of these latter bands and their photochemical behavior support their tentative identification as the ethyl-substituted derivative of **10** (hereafter called **11**).

Experiments with **9** gave a small yield of the **8** cation and a weak 444 nm band; studies with **8** gave a weak 453 nm band and experiments with **7** produced weak 453 and 444 nm bands. Owing to agreement with the 442 nm PDS band of **9**, the weak 444 and 453 nm bands are tentatively identified as the **9** cation.

Vibrational Structure. The matrix absorption spectra exhibit two intervals, one in the 1139–1182 cm^{-1} range and the other in the 330–415 cm^{-1} range, which are active in the vibronic absorption bands of the styrene cation and the five substituted styrene cations reported here. Aromatic in-plane C–H bending modes are found at 1178 cm^{-1} for benzene and 1180 cm^{-1} for styrene; in addition styrene exhibits a polarized Raman band at 1203 cm^{-1} which is due to the Ph–C stretching vibration.[19] The **3**-d_5 compound was prepared to characterize this vibrational mode; the interval decreased slightly from 1139 to 1098 cm^{-1} on d_5 substitution, consistent with a skeletal stretching mode and ruling out a C–H bending vibration. Accordingly, the 1139–1182 cm^{-1} intervals in Table I are assigned to Ph–C skeletal stretching vibrations. This mode should be active in both electronic transitions since conjugation between the two π systems is different for each electronic state.

The lower frequency mode observed twice in each red absorption decreased from about 415 cm^{-1} for **1**, p-CH$_3$-**1**, and **2** cations to 350 cm^{-1} for the **3** cation and 330 cm^{-1} for the **7** cation. The observation of such a pronounced substituent effect, particularly β-methyl and β-ethyl substitution, indicates that this mode involves the alkene skeleton. Styrene itself exhibits a bending mode at 440 cm^{-1}.[19] It is reasonable to expect Ph—C=C bending vibrations to be active in the "charge-transfer" transition since a change in electron density delocalization on the alkene group accompanies the transition, and the Ph—C=C skeletal angle may change due to reorganization of the conjugation between the two π systems.

Assignment of the other intervals to specific vibrational modes is difficult and uncertain for a complicated molecule like styrene. The 1478 cm^{-1} interval for the **3** cation probably corresponds to the ring skeletal stretching vibration observed as a polarized Raman band at 1446 cm^{-1} for styrene; the 1316 cm^{-1} interval in the **3**-d_5 cation spectrum supports this assignment. Intervals in the 704–764 cm^{-1} range may correspond to the mode responsible for a polarized Raman band at 772 cm^{-1} for styrene. The 1003 cm^{-1} interval in the ultraviolet band of the **3** cation probably corresponds to the symmetric ring breathing mode, observed as a strong, polarized 998 cm^{-1} Raman band for styrene; the displacement for the **3**-d_5 cation to 955 cm^{-1} is in agreement with the 957 cm^{-1} Raman shift for this mode in styrene-d_8.[19]

Rearrangements of Ions. Two types of cation rearrangements were observed in the present experiments: rearrangements that occurred between photoionization of precursor and freezing of the resulting cation in solid argon, and rearrangements upon mercury arc photolysis in the absorption band of the trapped ion. These rearrangements are summarized in Table III.

Since the precursor molecules have ionization energies near 8.5 eV, the 11.6–11.8 eV argon resonance photoionization employed here can impart up to about 3 eV of excess internal energy to some of the product molecular ions. In this event, the rearrangement process must compete with the quenching of internal energy by the condensing matrix. Six of the molecular ions produced in these experiments underwent such rearrangements.

Allylbenzene cation was expected to rearrange to the **3** cation since only the latter was found in PDS experiments;[1] a small yield

Table III. Summary of Molecular Cation Rearrangements Observed in Matrix Experiments with Phenyl Alkenes[a]

Between Photoionization and Condensation
$3 \rightarrow 10$
$4 \rightarrow 3$ and 10
$5 \rightarrow 3$ and 10
$7 \rightarrow 8$, 9, and 10
$8 \rightarrow 7$, 9, and 11
$9 \rightarrow 8$
During Photolysis of 20 K Sample
$10 \xrightarrow{420\text{ nm}} 3$ and 4
$4 \xrightarrow{290\text{ nm}} 3$, 6, and 10
$7 \xrightarrow{630\text{ nm}} 8$
$8 \xrightarrow{290\text{ nm}}$ (methylindan)$^{+\cdot}$ or (toluene)$^{+\cdot}$

[a] The numbers refer to the precursor as identified in the experimental section; it is, of course, radical cation rearrangements given here.

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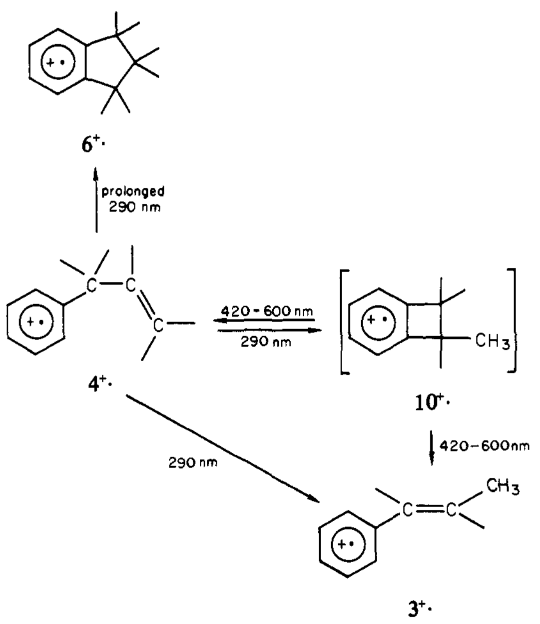
Scheme I



of the **3** cation was observed in the initial spectrum in experiments with **4**, as shown in Figure 4a; in addition, a new band system, possibly due to another rearrangement product **10** cation, was observed. Although rearrangement was not observed in PDS experiments with the **5** cation, both **3** and **10** cations were minor products in the **5** matrix experiments.

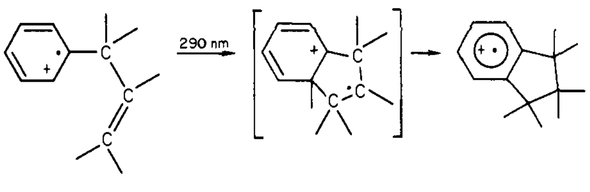
Each of the phenylbutenes **7** and **8** gave both the **7** and **8** cations and a new band system red shifted 14 nm from the **10** system, which is presumed to be due to the ethyl-substituted benzocyclobutane (**11**) cation. It is perhaps surprising that some $7^{+\cdot} \rightarrow 8^{+\cdot}$ and $7^{+\cdot} \rightarrow 9^{+\cdot}$ rearrangement of the double bond away from conjugation with the aromatic ring was observed, especially since the analogous $3^{+\cdot} \rightarrow 4^{+\cdot}$ process was not observed. However, a mass spectroscopic study of 1-phenylheptanes[20] demonstrates the ease of double bond migration after ionization and shows that the present matrix observation is reasonable.

Photolysis of allylbenzene cation with 290–1000 nm radiation gave rich rearrangement chemistry, summarized in Scheme I. Photolysis with 420–600 nm radiation covering the **10** cation absorption, but not the **4** cation absorption, produced rearrangement to both **4** and **3** cations. Brief 290–1000 nm photolysis covering the 400 nm **4** cation absorption increased **3** and **10** cation absorptions. Prolonged 290–1000 nm irradiation into all of the four $C_9H_{10}^+$ absorptions observed here, **3**, **4**, **5**, and **10** cations, increased the **3** cation absorptions at the expense of all others showing that the **3** configuration of olefin and aromatic π systems in conjugation produces the most stable arrangement for these molecular ions.

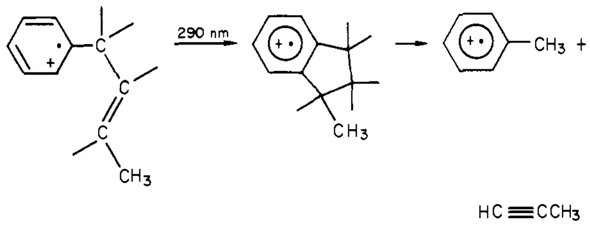
The production of the **6** cation from the **4** cation by ring closure during prolonged 290–1000 nm photolysis is of interest. Apparently interaction between the olefin π system and the hole in the aromatic π system is sufficient to produce indan cation upon activation by irradiation into the allylbenzene cation absorption at 400 nm. In effect, intramolecular electrophilic substitution occurs upon electronic excitation of the **4** cation, as depicted in Scheme II. A similar process has been observed in mass-spectroscopic studies with $(C_6H_5\text{-}CH_2CH_2CH_2\text{-}OH)^+$, which forms indan cation after elimination of water.[21]

An analogous photoinduced process occurs in experiments with **8**, but apparently the possible methyl-substituted indan cation product is less stable than the McLafferty rearrangement product,[22] which further isomerizes to the toluene cation under matrix photolysis,[5] Scheme III. There is, of course, the possibility that the methylindan cation absorbs at 430.5 nm as does the toluene cation. The fact that the toluene cation produced from cycloheptatriene by 450 nm radiation was virtually destroyed by further 290 nm photolysis[5,23] does suggest a less photosensitive species than the toluene cation found for the present new 430.5 nm product. Although a possible methylindan cation identification of the major product of Scheme III cannot be ruled out, the toluene cation is the more probable product.

Scheme II



Scheme III



Finally, no evidence was found in COT experiments for the **1** cation and likewise COT cation was not observed in experiments with **1**. Furthermore, the PDS of **1** and COT were distinctly different.[1] The six-to-eight membered ring expansion postulated to explain isotopic scrambling in the **1** cation in mass spectroscopic studies[24] apparently does not occur with the activation energy available in the argon matrix photoionization or in the ICR-PDS experiments.

Gas-Phase Comparisons. A comparison between the argon matrix absorption spectrum and the gas-phase PDS for the β-methylstyrene cation is of interest. The argon matrix solvent shifts the red and ultraviolet absorptions approximately 340 and 1460 cm^{-1} to lower energy, respectively, and reduces their full-widths at half-maximum to approximately 300 and 600 cm^{-1}, respectively, a factor of 6 sharper than the corresponding PDS bands.[1] As a consequence of sharper bands, matrix absorption spectra clearly distinguish between **3** and **7** cations, absorbing at 591.1 and 373.6 nm and 594.2 and 376.6 nm, respectively.

A major difference between the matrix-isolated cation and the cation in ICR-PDS experiments is excess internal energy. In the latter case, ions are produced by impacting electrons with an average of 1 eV more enery than required for ionization, which probably forms ions with some excess internal energy. In addition to the **3** cation absorptions, which are a factor of 6 sharper than PDS bands, toluene and *p*-xylene cation absorptions are more than an order-of-magnitude sharper in solid argon than the corresponding PDS bands.[5,23] It has been postulated that sharper matrix absorption bands are due to vibrationally relaxed ions in the matrix.[5] Furthermore, infrared spectra of large molecules in matrices are very sharp because the rotational temperatures are low, which should also sharpen the electronic spectra. Finally, lifetime broadening may affect the gaseous photodissociation bandwidths more than the matrix absorption bandwidths owing

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to faster vibrational relaxation and reduced internal conversion rate in the matrix.[5] In conclusion, quenching of internal energy by the matrix probably plays a major role in sharpening cation absorptions in the matrix environment.

The presence of excess internal energy in the **4** cation formed in the PDS experiment is demonstrated by its essentially complete rearrangement to the **3** cation.[1] On the other hand, the matrix photoionization experiment with **4** quenches many **4** cations quickly enough to trap at least comparable amounts of **3** and **4** cations, based upon the assumption that the absorption cross sections for the $\pi \rightarrow \pi$ transitions of **3** and **4** cations are similar.

Conclusions

The matrix photoionization technique produces phenylalkene molecular cations with absorption spectra slightly red shifted from PDS observations. In several cases, the matrix bands are sharp enough to resolve vibrational structure. Rearrangements of several molecular ions were observed during sample condensation and upon photolysis of the cold sample. Of particular interest, the allylbenzene cation was rearranged to the β-methylstyrene cation and the indan cation by 290 nm radiation. The matrix absorptions are substantially sharper than PDS bands, which suggests that the PDS bandwidth may, in part, be due to excess internal energy in the molecular ions produced by electron impact. It is perhaps noteworthy that the allylbenzene cation rearranges completely to the β-methylstyrene cation in PDS experiments, but a substantial fraction of the allylbenzene cation formed in matrix photoionization experiments is quenched and trapped in the matrix.

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Perfluoroacetylmethylmethylene and Its Quintet Radical Pair: Isolation and ESR Detection

H. Murai, J. Ribo, M. Torres, and O. P. Strausz*

Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2. *Received September 5, 1980*

Abstract: Perfluoroacetylmethylmethylene (**1**) was produced by the photolysis of 3-diazohexafluoro-2-butanone at $T < 30$ K. Two triplet ESR spectra were observed with relative intensities of ca. 9:1 and assigned to the cis and trans geometrical conformers of **1**, respectively. These triplets are most likely the ground electronic state of **1**. The relative yields of the conformers appear to be governed by the geometry of the source compound. *cis*-**1** is kinetically more stable than *trans*-**1** and decays at a higher temperature featuring first-order kinetics with $E_a = 5.0$ kcal/mol, probably corresponding to triplet → singlet intersystem crossing prior to or concertedly with a Wolff rearrangement to the ketone structure. An additional weak ESR spectrum attributed to a quintet state radical pair arising from the interaction of two triplet **1** was also observed.

The existence of geometrical isomerism in triplet carbenes having an α double bond and frozen in low-temperature matrices was first demonstrated for the case of naphthylmethylenes with the use of ESR spectroscopy by Trozzolo, Wasserman, and Yager.[1] Since then cis/trans conformer pairs have been detected in the triplet state of several other α-unsaturated carbenes including vinylmethylene[2] (**2**), carbomethoxymethylene[3] (**3**), carboethoxymethylene[3] (**4**), iminocyclohexadienylidene,[4] benzoylphenylmethylene[5,6] (**5**), and dibenzoylmethylene.[7] Thiobenzoylphenylmethylene[8] prepared recently by the photolysis of 4,5-diphenyl-1,2,3-thiadiazole appeared to be present only as the cis isomer: this was attributed to the controlling effect of the geometry of the precursor molecule on the product carbene geometry.

In previous studies on triplet benzoylphenylmethylene[5,6] and triplet 9-oxo-10-anthrylene[9] we have observed in each case a new quintet state ESR spectrum, in addition to the triplet spectrum. These we assigned to a stable, quintet state radical pair formed by the interaction of two close neighbor triplet carbenes. Prior to these studies, radical pairs had not been detected in higher than triplet multiplicity although contemporaneously the existence of a short-lived quintet state radical pair has been reported.[10]

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