These results are completely described by considerations of (a) the size and shape sorption selectivity of the pentasil zeolites, (b) the sorption of water by the hydrophilic sites of the pentasil zeolites (due to the presence of Al atoms and their associated cations), and (c) the hydrophobic characteristics of the pentasil channels which do not contain an Al atom. The above ideas are summarized in Figures 4, 5, 6, and 7.

Experimental Section

Photolysis Experiments. The zeolite samples were activated at 550 °C for at least 1 h prior to use. For a typical photolysis experiment, an activated sample was charged with a minimum amount of dry *n*-pentane (with care taken to minimize the time in which the sample was exposed to the atmosphere), and then 1.0 mg of ketone in 0.5 mL of *n*-pentane was added to the sample. The bulk of the solvent was removed by placing the sample in a stream of warm (50 °C), dry air. The solid was subsequently placed into a quartz photolysis cell, equipped with a side arm which allowed for vacuum degassing. The dry samples were degassed to a pressure of 2×10^{-4} torr. For the photolysis experiments involving dry samples, the latter was maintained under vacuum and tumbled during photolysis at ambient temperature. A 400-W medium-pressure Hanovia Hg lamp was employed as the light source with an aqueous K_2CrO_4 (10-mm) filter employed to isolate the 313-nm line. For the preparation of the wet samples, the sample cell was connected to a vacuum line on which a reservoir of water served as the source of water vapor. The whole line was throughly degassed via the freeze-thaw method before the water vapor was admitted to the sample. The amount of water adsorbed by the zeolite sample was controlled by the time of exposure and was determined by weighing of the sample. The resulting sample was tumbled during photolysis as described above. After irradiation, the sample was soaked in 6 mL of benzene overnight. Analysis of the filtered sample was performed by vapor phase chromatographic analysis on a Varian 3700 gas chromatograph equipped with a 50-m SE-30 capillary column at 180 °C. The areas of the peaks in the GC traces were integrated on a Hewlett-Packard 3390 integrator. The cage effect was found to be independent of ketone coverage up to at least 20% by weight; however, in the experiments reported, the coverage was maintained at ca. 1% (1 mg of ketone/100 mg of zeolite).

For the isooctane washing experiments the samples were prepared in a manner described above. The sample was soaked in isooctane (6 mL) for 1 min and then filtered, and the filtrate was subjected to vapor phase chromatographic analysis as described above.

Benzene (Fischer spectroanalyzed), *n*-pentane (EM, Omnisolv), and isooctane (MCB, Omnisolv) were used without further purification. 1-(4-Methylphenyl)-3-phenylpropan-2-one (*p*-MeDBK, *p*-ACOB) was prepared by a literature procedure.[18] 1-(2-Methylphenyl)-3-phenylpropan-2-one (*o*-MeDBK, *o*-ACOB) was prepared by a modification of the same procedure.

Samples of Na, TPA-ZSM-5 with Si:Al = 20, 40, and 80, were prepared by the methods of Rollman and Volyocsik,[19] calcined in flowing air at 60 °C/h to 550 °C, and then held at 550 °C for 10 h. The samples were then exchanged 3 times with a 10% NH_4NO_3 solution at 90 °C for 1 h and calcined as described above to give the acid form. The materials were then exchanged 3 times with a 10% $NaNO_3$ solution at 90 °C for 1 h, dried, and recalcined as above. A sample of ZSM-5 (Si:Al = 70) was a gift of the Mobil Corp.

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1,2,4,6-Cycloheptatetraene: The Key Intermediate in Arylcarbene Interconversions and Related C_7H_6 Rearrangements

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Abstract: Thermolysis or photolysis of phenyldiazomethane (**2**) produces phenylmethylene (**3**), which ring-expands to give 1,2,4,6-cycloheptatetraene (**6**). Spectroscopic and chemical evidence rule out bicyclo[4.1.0]hepta-2,4,6-triene (**4**), cycloheptatrienylidene (**5**), and bicyclo[3.2.0]hepta-1,3,6-triene (**11**) intermediates. The strained allene in cycloheptatetraene (**6**) exhibits infrared absorptions at 1824 and 1816 cm^{-1}. Deuterium substitution produces the expected 10-cm^{-1} shift in the allene absorption. Fluorine or chlorine substitution substantially enhances the allene absorption intensity. Deuterium labeling studies reveal that the intramolecular chemistry of cycloheptatetraene (**6**) involves reversible thermal or photochemical equilibration with phenylmethylene (**3**). The intermolecular chemistry of **6** involves dimerization. At temperatures as low as 10 K, **6** forms a labile [2 + 2] dimer, **7**, which undergoes thermally allowed, electrocyclic ring opening to give heptafulvalene (**8**) upon warming to room temperature. The rearrangements of 7-acetoxynorbornadiene (**9**), 2-diazobicyclo[3.2.0]hepta-3,6-diene (**31**), and 8-diazobicyclo[2.2.2]octa-2,5-dien-7-one (**33**) all involve cycloheptatetraene (**6**) intermediates.

The opposing tendencies of arylcarbenes and nitrenes to preserve their aromaticity and to seek restoration of tetravalency result in a singularly fascinating series of multiple rearrangements.[2] A detailed understanding of the mechanisms involved is of importance from the point of view of both basic science and industrial

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(2) (a) Jones, W. M.; Brinker, U. H. In *Pericyclic Reactions*; Marchand, A. P., Lehr, R. E., Eds.; Academic: New York, 1977; Vol. 1, Chapter 3. (b) Jones, W. M. In *Rearrangements in Ground and Excited States*; deMayo, P., Ed.; Academic: New York, 1980; Vol. 1, Chapter 3. (c) Wentrup, C. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum: New York, 1980; Vol. 1, Chapter 4. (d) Wentrup, C. *Reactive Molecules*; Wiley-Interscience: New York, 1984; Chapter 4.

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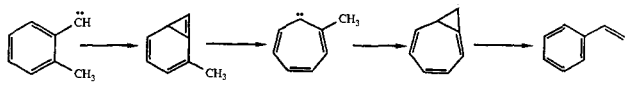
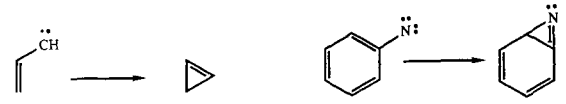
technology. Very high temperature thermal cracking of industrially important alkylaromatics involves arylcarbene intermediates.[3,4]

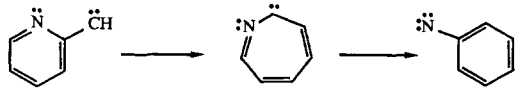
Twenty years ago, Vander Stouw and Shechter postulated the first arylcarbene ring-expansion mechanism to account for styrene formation upon thermolysis of *o*-tolyldiazomethane.[5]



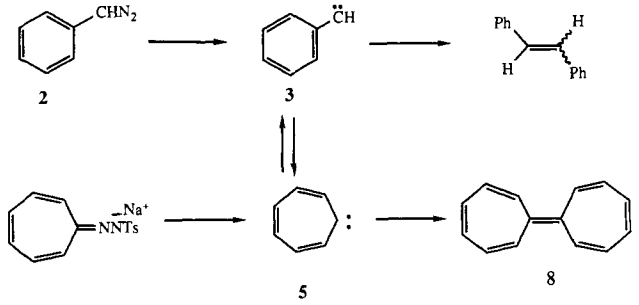
Two studies provided precedence for the initial cyclization step. Closs established the cyclization of vinylmethylene to cyclopropene,[6] and Huisgen proposed the cyclization of phenylnitrene to the azirine.[7] (Huisgen's proposal has since been shown to be wrong.[8])



In 1968, Wentrup presented the first evidence for reversibility of the ring-expansion step by demonstrating the interconversion of 2-pyridylmethylene and phenylnitrene.[9]

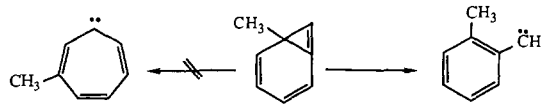


Shortly thereafter, W. M. Jones demonstrated ring expansion in the parent phenylmethylene system. Jones argued for cycloheptatrienylidene (**5**) as the key intermediate based on (1) isolation of heptafulvalene (**8**) from the thermolysis of phenyldiazomethane



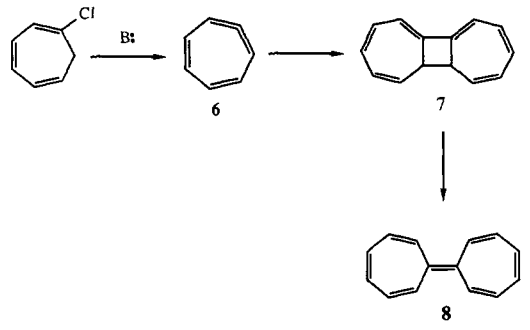
(**2**)[10] and (2) isolation of heptafulvalene (**8**) from thermolysis or photolysis of tropone tosylhydrazone sodium salt.[11] Again, Wentrup established the reversibility of the ring expansion by isolating stilbenes from thermolysis of tropone tosylhydrazone sodium salt.[12] Baron, M. Jones, and Gaspar revealed the intricate multiple carbene rearrangements that arise as a consequence of this reversible ring-expansion process in the tolylmethylene series.[13]

Both Wentrup and W. M. Jones considered the ring expansion to occur directly, rather than through a bicyclo[4.1.0]hepta-2,4,6-triene (**4**) intermediate. Wentrup argued against bicyclo[4.1.0]hepta-2,4,6-triene (**4**) involvement in the thermal rearrangement on thermochemical grounds.[14] Billups generated 1-methylbicyclo[4.1.0]hepta-2,4,6-triene in solution and showed that it rearranged to *o*-tolylmethylene.[15]

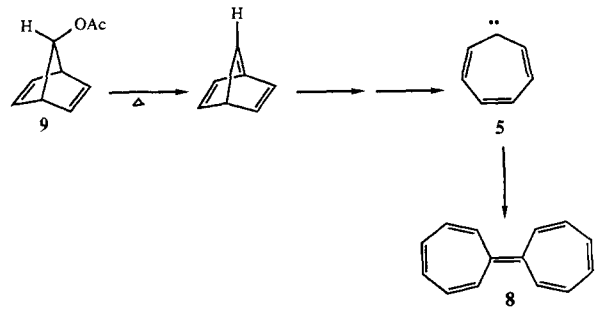


He obtained no direct evidence for ring expansion. He noted, however, that the reaction displays a poor mass balance.

Other precursors to C_7H_6 isomers exist. Untch proposed that base-induced dehydrohalogenation of an isomeric mixture of chlorocycloheptatrienes generates 1,2,4,6-cycloheptatetraene (**6**).[16]



He further suggested that heptafulvalene (**8**) formation could be accounted for by [2 + 2] dimerization of cycloheptatetraene (**6**) followed by thermally allowed electrocyclic ring opening of **7**. Thus, heptafulvalene formation cannot necessarily be taken as evidence for cycloheptatrienylidene (**5**). Hoffmann et al. reported that thermolysis of 7-acetoxynorbornadiene (**9**) ultimately leads



to cycloheptatrienylidene (**5**), on the basis of isolation of heptafulvalene (**8**).[17] However, in view of Untch's suggestion, a cycloheptatetraene (**6**) intermediate cannot be ruled out. W. M. Jones observed the foiled methylene rearrangement of 7-norbornadienylidene (**10**) to bicyclo[3.2.0]hepta-1,3,6-triene (**11**).[18] At 300 °C, **11** apparently crosses into the cycloheptatetraene/cycloheptatrienylidene manifold. Heptafulvalene (**8**) is the isolable product.

Both semiempirical[19,20] and ab initio[21] calculations predict singlet cycloheptatetraene (**6**) to lie 16–48 kcal/mol below singlet

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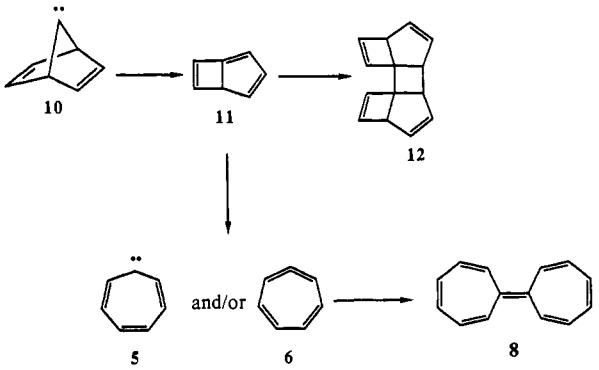
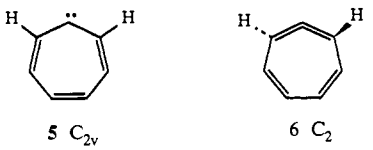
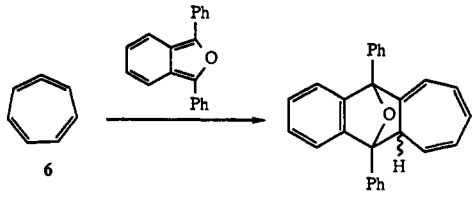
(21) Radom, L.; Schaefer, H. F.; Vincent, M. A. *Nouv. J. Chim.* **1980**, *4*, 411–415.



cycloheptatrienylidene (**5**). Waali's MNDO calculation does not

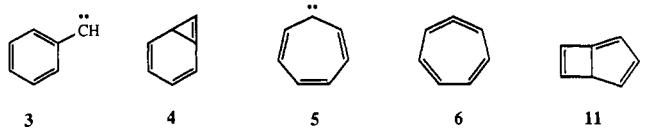


find singlet cycloheptatrienylidene (**5**) to be an energy minimum.[19] Rather, it finds **5** to be the transition state that interconverts the enantiomeric cycloheptatetraenes. In addition, almost all cycloheptatrienylidene trapping studies can be explained equally well in terms of cycloheptatetraene.[22] However, the current wisdom holds that singlet cycloheptatrienylidene is a discreet intermediate and that it thermally equilibrates with cycloheptatetraene (**6**).[22] Kirmse's ethanol trapping study seems to be best interpreted in this way.[23] Saito et al. demonstrated the thermal conversion of **5** to **6** by decomposing tropone tosylhydrazone sodium salt in solution and trapping cycloheptatetraene (**6**) with diphenylisobenzofuran.[24] In a related trapping study, W. M. Jones demonstrated the chirality of the allene moiety in cycloheptatetraene.[22b]



We shun the temptation to draw parallels between the parent C_7H_6 system and the plethora of substituted and benzannelated arylcarbene systems that have been studied.[2] The annelated systems are, in fact, poor models for the parent system. We find that the photochemistry of the naphthylmethylenes[25] shows a striking contrast to that of the phenylmethylenes.[26] This situation occurs in the naphthylnitrene/phenylnitrene series as well.[27]

In this paper, we investigate the roles of phenylmethylene (**3**), bicyclo[4.1.0]hepta-2,4,6-triene (**4**), cycloheptatrienylidene (**5**), 1,2,4,6-cycloheptatetraene (**6**), and bicyclo[3.2.0]hepta-1,3,6-triene (**11**) in C_7H_6 rearrangements. We describe in detail the characterization of phenylmethylene (**3**) and its thermal and photochemical rearrangement product, 1,2,4,6-cycloheptatetraene (**6**). We discuss the role of cycloheptatetraene in the arylmethylene interconversions. In addition, we present several novel precursors to cycloheptatetraene. This chemistry, when coupled with the recent characterization of triplet cycloheptatrienylidene (**5**),[28] reveals many subtleties of rearrangements on the C_7H_6 energy surface.



Results

Structural Assignments. The detailed arguments concerning the interpretation of infrared spectra and the structural assignment of 1,2,4,6-cycloheptatetraene are presented in the Discussion section.

Phenylmethylene (3). Irradiation (>478 nm, 3700 min) of argon matrix-isolated phenyldiazomethane (**2**) produces triplet phenylmethylene (**3**): IR (Ar, 15 K) 3078 w, 740 s, 670 s, 445 m cm^{-1}; UV (Ar, 12 K) λ_{max} 430, 423, 419, 416, 412, 409, 405, 402, 400, 397, 386, 381, 372, 245, 240 nm (Figure 1); ESR (Ar, 10 K) $|D/hc| = 0.519$, $|E/hc| = 0.0248$ cm^{-1}; Z_1 2210, X_2 4885, Y_2 5916, Z_2 8850 G; microwave frequency 9.30 GHz. Irradiation (>470 nm, 1237 min) of **2** in a carbon monoxide doped argon matrix (0.25% CO in Ar) generates phenylmethylene (**3**) and a small amount of phenylketene (**13**) (2115 cm^{-1}). The infrared bands of CO and **3** disappear, and the infrared bands of phenylketene (**13**) (2115 s, 1502 s, 750 s, 690 s cm^{-1}) increase upon warming the matrix to the softening point (ca. 40 K).

The ESR zero-field splitting parameters of phenylmethylene (**3**) agree with the literature values.[29] The carbene exhibits the weak π,π^* transitions with the extensive vibronic coupling characteristic of triplet arylcarbenes[30] and the benzyl radical.[31] The infrared spectrum demonstrates that the monosubstituted aryl ring remains intact, while excluding photoisomerization to phenyldiazirine (**1**). The carbon monoxide trapping experiment provides chemical evidence for the carbene assignment. The identity of the trapping product **13** was established by comparison of the infrared spectrum with that of the authentic material prepared by Wolff rearrangement of diazoacetophenone (**14**).

1,2,4,6-Cycloheptatetraene (6). Photolysis (>416 nm) of phenylmethylene (**3**) results in the total disappearance of the IR and UV absorptions of **3** as well as a dramatic decrease in the ESR signal. The IR spectrum ((Ar, 15 K) 3040 m, 3014 m, 1824 w, 1816 w, 1380 m, 1270 w, 912 w, 771 s, 690 m, 679 s, 582 m, 407 w cm^{-1}) and rather nondescript UV spectrum ((Ar, 15 K) no λ_{max}, tail out to 390 nm) (Figure 1) of 1,2,4,6-cycloheptatetraene (**6**) appear.[32] Irradiation (>279 nm) of this species produces no discernable change in the IR or UV spectra. The persistent, triplet ESR signal reveals a small, steady-state concentration of phenylmethylene. Flash vacuum thermolysis (375 °C, 100% conversion) of **2** followed by cocondensation of the pyrolysate with argon produces only cycloheptatetraene (**6**), as observed by infrared spectroscopy. No triplet ESR signal is observed under these conditions.[33a] Subsequent irradiation (>278 nm) leads to a rapid buildup of a small steady-state concentration

(22) For a critical discussion of this point, see: (a) Balci, M.; Winchester, W. R.; Jones, W. M. *J. Org. Chem.* **1982**, *47*, 5180–5186. (b) Harris, J. W.; Jones, W. M. *J. Am. Chem. Soc.* **1982**, *104*, 7329–7330.

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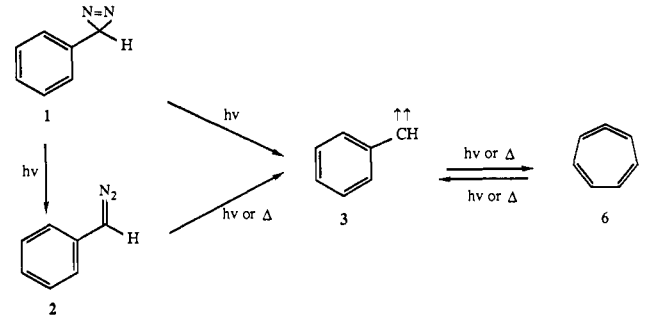
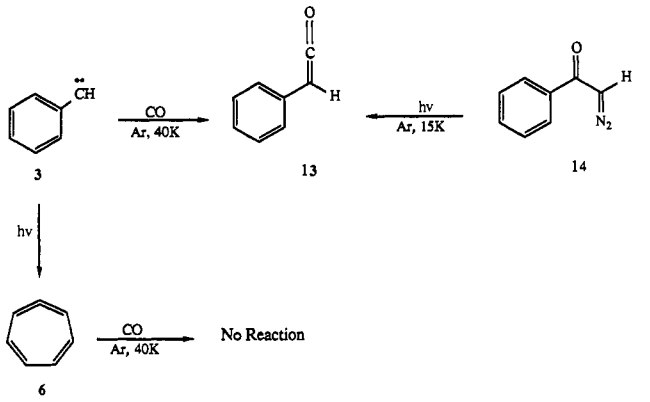
(32) The UV spectrum of cycloheptatetraene (**6**) published previously[26] is incorrect. The earlier spectrum, obtained upon irradiation (>336 nm) of phenyldiazirine (**1**), contains phenyldiazomethane (**2**) ($\lambda_{max} \sim 275$ nm), phenylmethylene (**3**) ($\lambda_{max} \sim 245$ nm), and cycloheptatetraene (**6**). As shown in Figure 1, cycloheptatetraene does not exhibit a characteristic λ_{max}.

(33) (a) Doublet radicals ($\cdot CH_3$) are observed. (b) Doublet radicals ($\cdot CH_3$ and $\cdot CH_2D$) are observed.

Scheme I



Scheme II



of triplet phenylmethylene (**3**).[34] Increasing the thermolysis temperature leads to secondary rearrangements. At 755 °C, only fulvenallene (**15**) (IR (Ar, 15 K) 1978 w, 1971 w, 1968 m, 1945 s, 1937 w, 1913 s, 1478 s, 1371 m, 1068 m, 879 s, 838 s, 750 s, 601 m cm^{-1}) and the ethynylcyclopentadienes (**16**) (IR (Ar, 15 K) 3318 m, 2098 w, 1371 w, 671 s, 636 m cm^{-1}) are observed. The assignments for **15** and **16** are based on comparison with the literature IR spectra.[35]

Cycloheptatetraene (**6**) does not react with carbon monoxide. Irradiation (>364 nm) of phenyldiazomethane (**2**) in a carbon monoxide doped argon matrix (0.24% CO in Ar) generates **6**. Warming the matrix produces no change in the IR spectrum.

We examined the dimerization chemistry of cycloheptatetraene under three different conditions.

(1) Irradiation (>416 nm) of matrix-isolated phenyldiazomethane (**2**) produced cycloheptatetraene (**6**). The argon matrix was carefully pumped away at 40–50 K. After the cryostat warmed to room temperature under an atmosphere of argon, the dimer was rinsed off of the window with $CDCl_3$. GC–MS and ^1H NMR analyses showed the dimeric products to be *cis*- and *trans*-stilbenes and heptafulvalene (**8**). Some oxygen incorporation products were also observed.

(2) Flash vacuum thermolysis (370 °C, 100% conversion) of phenyldiazomethane (**2**) followed by cocondensation with argon produced cycloheptatetraene (**6**). Decomposition of the matrix, as before, yielded the dimer. GC–MS and ^1H NMR analyses showed heptafulvalene (**8**) to be the sole product.

(3) Flash vacuum thermolysis (370 °C, 100% conversion) of phenyldiazomethane (**2**) followed by trapping directly on a cold window at 10 K (*no argon*) did not produce cycloheptatetraene (**6**). The observed IR spectrum ((neat 10 K) 3023 m, 2920 w, 2855 w, 1562 m, 970 w, 715 s, 688 m, 480 s cm^{-1}) (Figure 2) is similar to that of heptafulvalene, but the UV–vis spectrum ((neat, 10 K) λ_{max} 455, 360 sh, 300, 240 nm) (Figure 3) is not. However, warming this material to room temperature under an atmosphere of argon produced heptafulvalene (**8**) (Figures 2 and 3). The identity of **8** was confirmed by comparison of the IR, UV, ^1H NMR, and GC–MS data with those of the freshly prepared authentic material.[11]

Figure 1. Bottom: Ultraviolet spectrum of phenyldiazomethane (**2**) matrix isolated in argon at 15 K. Middle: Ultraviolet spectrum of phenylmethylene (**3**) formed upon irradiation (>470 nm, 2340 min) of phenyldiazomethane matrix isolated in argon at 15 K. Top: Ultraviolet spectrum of 1,2,4,6-cycloheptatetraene (6) formed upon irradiation (>-415 nm, 1140 min) of phenylmethylene matrix isolated in argon at 15 K.

Phenyldiazirine (1). Irradiation (>338 nm, 20 min) of argon matrix-isolated phenyldiazirine (**1**) produces phenyldiazomethane (**2**) (IR (Ar, 15 K) 2080 cm^{-1}; UV (Ar, 15 K) λ_{max} 274 nm), phenylmethylene (**3**) (IR and UV (Ar, 15 K), vide supra), and a small amount of cycloheptatetraene (**6**) (IR and UV (Ar, 15 K, vide supra).[32] Further irradiation (>470 nm) converts phenyldiazomethane (**2**) to phenylmethylene (**3**) (IR and UV (Ar, 15 K), vide supra). Shorter wavelength photolysis (>415 nm) results in the total disappearance of the IR and UV absorptions of **3** and production of **6**.

Diazoacetophenone (14). Irradiation (>364 nm, 167 min) of argon matrix-isolated diazoacetophenone (**14**) produces phenylketene (**13**) (IR (Ar, 15 K) 2118 s, 1607 m, 1508 m, 1238 w, 1027 w, 751 m, 704 w, 691 m, 662 w, 508 w, 460 w cm^{-1}).

(34) Two pieces of evidence convince us that no residual diazo compound remains after thermolysis onto the ESR sample tip. First, long-wavelength irradiation (>470 nm) of the ESR matrix after thermolysis does not generate a triplet carbene signal. Second, the corresponding IR experiments do not show diazo compound when carried out at equal temperatures.

(35) Fulvenallene: Hedaya, E.; Kent, M. E. *J. Am. Chem. Soc.* **1970**, *92*, 2149–2151. Spangler, R. J.; Beckmann, B. G.; Kim, J. H. *J. Org. Chem.* **1977**, *42*, 2989–2996. Angell, C. L. *J. Mol. Struct.* **1971**, *10*, 265–273. Ethynylcyclopentadiene: Hedaya, E.; Kent, M. E. *J. Am. Chem. Soc.* **1970**, *92*, 2149–2151.

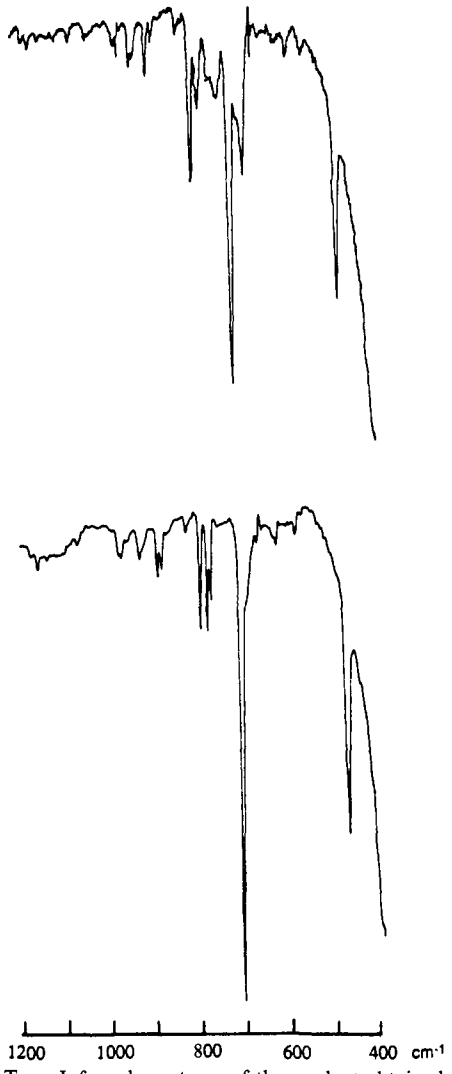


Figure 2. Top: Infrared spectrum of the product obtained upon flash vacuum thermolysis (370 °C) of phenyldiazomethane (**2**) followed by condensation of the pyrolyzate directly onto a cold window at 10 K with no argon. Bottom: Infrared spectrum of heptafulvalene (**8**) formed by warming the thermolysis product to room temperature in an atmosphere of argon.

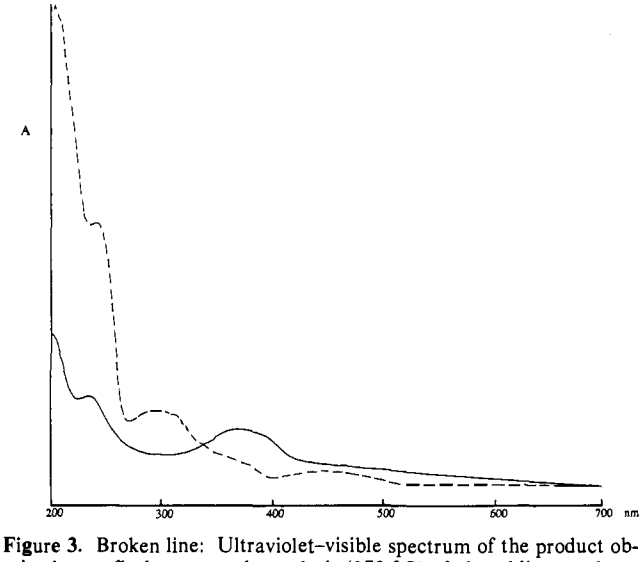


Figure 3. Broken line: Ultraviolet–visible spectrum of the product obtained upon flash vacuum thermolysis (370 °C) of phenyldiazomethane (**2**) followed by condensation of the pyrolyzate onto a cold window at 10 K with no argon. Solid line: Ultraviolet–visible spectrum of heptafulvalene (**8**) formed by warming the thermolysis product to 80 K over 30 min.

α-Deuteriophenyldiazomethane (18a). Irradiation (>478 nm, 2105 min) of argon matrix-isolated α-deuteriophenyldiazomethane (**18a**) produces triplet α-deuteriophenylmethylene (**22a**): IR (Ar, 10 K) 3075 m, 3038 w, 2960 w, 2929 w, 2842 w, 1500 m, 1461 m, 1449 m, 1427 m, 1265 m, 1088 m, 1013 m, 751 m, 740 s, 666 s, 480 m cm^{-1}; ESR (Ar, 10 K) $|D/hc| = 0.521$, $|E/hc| = 0.0263$ cm^{-1}; Z_1 2227, X_2 4860, Y_2 5953, Z_2 8865 G; microwave frequency 9.31 GHz. Irradiation (>416 nm) of the carbene leads to a sharp decrease in intensity of the ESR signal. The simple infrared spectrum of a monosubstituted aromatic species is replaced by the more complicated spectrum of 1-deuteriocycloheptatetraene (**26a**): IR (Ar, 10 K) 3050 w, 3019 m, 1822 w, 1811 w, 1501 m, 1381 m, 1038 m, 919 w, 781 m, 724 s, 690 m, 683 m, 620 s, 572 m cm^{-1}. Flash vacuum thermolysis of **18a** (490 °C, 100% conversion) followed by cocondensation with argon generates a mixture of deuteriocycloheptatetraene isomers but no carbene (by ESR).[33b] Subsequent irradiation (>278 nm) rapidly gives a weak ESR signal due to a mixture of deuteriophenylmethylene isomers.[34]

***o*-Deuteriophenyldiazomethane (19a).** Irradiation (>478 nm, 2233 min) of argon matrix-isolated *o*-deuteriophenyldiazomethane (**19a**) produces triplet *o*-deuteriophenylmethylene (**23a**): IR (Ar, 10 K) 3085 m, 1429 m, 934 m, 772 m, 751 s, 742 s, 733 m, 670 m, 630 m, 609 s, 442 s, 433 s cm^{-1}; ESR (Ar, 10 K) $|D/hc| = 0.519$, $|E/hc| = 0.0249$ cm^{-1}; Z_1 2213, X_2 4885, Y_2 5919, Z_2 8849 G; microwave frequency 9.309 GHz.[36] Irradiation (>416 nm) of the carbene leads to a sharp decrease in intensity of the ESR signal. The simple infrared spectrum of an ortho-disubstituted aromatic species is replaced by a complex spectrum consisting of 1-deuteriocycloheptatetraene (**26a**) (IR (Ar, 10 K) vide supra) and 4-deuteriocycloheptatetraene (**27a**): IR (Ar, 10 K) 3090 m, 3040 m, 3020 m, 1822 w, 1815 w, 1483 m, 788 s, 774 s, 755 s, 681 s, 639 s, 630 m, 579 m, 440 w, 405 m cm^{-1}. Continued irradiation (>278 nm) ultimately produces a small amount of 5-deuteriocycloheptatetraene (**28a**): IR (Ar, 15 K) vide infra. Flash vacuum thermolysis of **19a** (500 °C, 100% conversion) followed by cocondensation with argon generates a mixture of deuteriocycloheptatetraene isomers but no carbene (by ESR).[33b] Subsequent irradiation (>278 nm) rapidly gives a weak ESR signal due to a mixture of deuteriophenylmethylene isomers.[34]

***m*-Deuteriophenyldiazomethane (20a).** Irradiation (>478 nm, 2833 min) of argon matrix-isolated *m*-deuteriophenyldiazomethane (**20a**) produces triplet *m*-deuteriophenylmethylene (**24a**): IR (Ar, 10 K) 3060 m, 1448 m, 1040 w, 980 w, 970 m, 925 m, 800 m, 780 s, 738 m, 670 m, 649 s, 430 s cm^{-1}; ESR (Ar, 10 K) $|D/hc| = 0.518$, $|E/hc| = 0.0248$ cm^{-1}; Z_1 2210, X_2 4884, Y_2 5917, Z_2 8850 G; microwave frequency 9.274 GHz.[36] Irradiation (>416 nm) of the carbene leads to a sharp decrease in intensity of the ESR signal. The infrared spectrum of a meta-disubstituted aromatic species is replaced by a complex spectrum consisting of 4-deuteriocycloheptatetraene (**27a**) (IR (Ar, 10 K), vide supra) and 5-deuteriocycloheptatetraene (**28a**): IR (Ar, 10 K) 3079 m, 3030 m, 3008 m, 1820 w, 1814 w, 1380 m, 1330 m, 1262 m, 899 m, 870 m, 829 m, 811 m, 803 m, 771 m, 740 s, 683 s, 637 s, 608 m, 580 m, 554 m cm^{-1}. Flash vacuum thermolysis of **20a** (515 °C, 100% conversion) followed by cocondensation with argon generates a mixture of deuteriocycloheptatetraene isomers but no carbene (by ESR).[33b] Subsequent irradiation (>278 nm) rapidly gives a weak ESR signal due to a mixture of deuteriophenylmethylene isomers.[34]

***p*-Deuteriophenyldiazomethane (21a).** Irradiation (>478 nm, 2154 min) of argon matrix-isolated *p*-deuteriophenyldiazomethane (**21a**) produces triplet *p*-deuteriophenylmethylene (**25a**): IR (Ar, 10 K) 3069 m, 828 s, 606 m, 578 s, 432 s cm^{-1}; ESR (Ar, 10 K) $|D/hc| = 0.519$, $|E/hc| = 0.0247$ cm^{-1}; Z_1 2211, X_2 4887, Y_2 5917, Z_2 8946 G; microwave frequency 9.274 GHz. Irradiation (>416 nm) of the carbene leads to a decrease in intensity of the ESR signal. The simple infrared spectrum of a para-disubstituted aromatic species is replaced by the more complicated spectrum of 5-deuteriocycloheptatetraene (**28a**): IR (Ar, 15 K) vide supra.

(36) Deuterium substitution does not sufficiently perturb the system to render the rotational isomers distinguishable by ESR spectroscopy.

Continued irradiation (>278 nm) produces a small amount of both 1- and 4-deuteriocycloheptatetraene (**26a** and **27a**): IR (Ar, 15 K) vide supra. Flash vacuum thermolysis of **21a** (450 °C, 100% conversion) followed by cocondensation with argon generates a mixture of deuteriocycloheptatetraene isomers (by IR) but no carbene (by ESR).[33b] Subsequent irradiation (>278 nm) rapidly gives a weak ESR signal due to a mixture of deuteriophenylmethylene isomers.[34]

3-Fluoro-3-phenyldiazirine (17b). Irradiation (>338 nm) of argon matrix-isolated 3-fluoro-3-phenyldiazirine (**17b**) rapidly produces phenylfluoromethylene (**22b**) [IR (Ar, 15 K) 1595 s, 1450 m, 1311 m, 1222 s, 1164 s, 1107 s, 1082 s, 1061 s, 1020 m, 834 m, 758 s, 690 m, 678 m, 623 m cm^{-1}] and phenylfluorodiazomethane (**18b**) [IR (Ar, 15 K) 2022 s, 1501 m, 1264 m, 742 m cm^{-1}]. Upon long-wavelength irradiation (>470 nm), phenylfluorodiazomethane (**18b**) decomposes to phenylfluoromethylene (**22b**). Short-wavelength irradiation (>212 nm) of phenylfluoromethylene (**22b**) slowly produces 1-fluorocycloheptatetraene (**26b**): IR (Ar, 15 K) 3060 w, 3025 w, 1810 m, 1528 w, 1502 m, 1460 w, 1443 m, 1403 s, 1388 m, 1248 m, 1228 m, 1188 s, 1182 s, 937 m, 839 w, 823 m, 789 m, 759 m, 732 s, 661 w, 598 w, 532 w, 474 w cm^{-1}. Flash vacuum thermolysis of **17b** (325 °C, 100% conversion) followed by cocondensation with argon produces phenylfluoromethylene (**22b**), 1-fluorocycloheptatetraene (**26b**), and at least one unidentified compound, as observed by IR spectroscopy.

***o*-Fluorophenyldiazomethane (19b).** Irradiation (>416 nm) of argon matrix-isolated *o*-fluorophenyldiazomethane (**19b**) generates 1-fluorocycloheptatetraene (**26b**): IR (Ar, 15 K) vide supra (Figure 4). Shorter wavelength irradiation (>279 nm) of **26b** produces a small amount of phenylfluoromethylene (**22b**): IR (Ar, 15 K) vide supra. In a similar manner, flash vacuum thermolysis of **19b** (375 °C, 100% conversion) followed by cocondensation with argon gives a mixture of **22b** and **26b** as observed by IR spectroscopy.

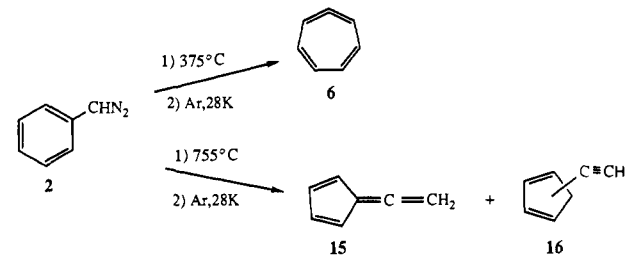
α-Deuterio-*o*-fluorophenyldiazomethane (29). Irradiation (>416 nm) of argon matrix-isolated α-deuterio-*o*-fluorophenyldiazomethane (**29**) generates 3-deuterio-1-fluorocycloheptatetraene (**30**): IR (Ar, 15 K) 3050 w, 3018 w, 2255 w, 1799 m, 1496 s, 1453 m, 1433 s, 1397 s, 1345 m, 1252 w, 1222 s, 1192 w, 1183 s, 1120 w, 1084 w, 950 w, 827 m, 776 m, 757 s, 747 s, 690 m, 633 m, 587 w, 512 w cm^{-1}.

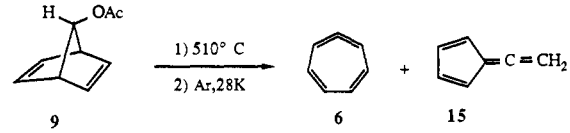
3-Chloro-3-phenyldiazirine (17c). Irradiation (λ = 372–392 nm) of argon matrix-isolated 3-chloro-3-phenyldiazirine (**17c**) produces phenylchloromethylene (**22c**) [IR (Ar, 15 K) 1600 m, 1582 s, 1477 w, 1440 m, 1318 w, 1301 m, 1244 m, 1222 s, 1168 s, 995 w, 840 s, 761 s, 744 s, 671 s, 563 m cm^{-1}][37] and a small amount of phenylchlorodiazomethane (**18c**) [IR (Ar, 15 K) 2042 cm^{-1}]. Long-wavelength irradiation (>470 nm) causes the 2042-cm^{-1} band of **18c** to disappear. Prolonged irradiation (>338 nm) of **22c** generates 1-chlorocycloheptatetraene (**26c**): IR (Ar, 15 K) 1809 m, 1425 w, 1360 w, 1222 w, 1061 s, 920 m, 881 w, 798 s, 726 s, 714 s, 590 w, 553 w, 497 w cm^{-1}. Flash vacuum thermolysis of **17c** (400 °C, 100% conversion) followed by cocondensation with argon produces phenylchloromethylene (**22c**), 1-chlorocycloheptatetraene (**26c**), and at least one unidentified compound, as observed by IR spectroscopy.

***o*-Chlorophenyldiazomethane (19c).** Irradiation (>364 nm) of argon matrix-isolated *o*-chlorophenyldiazomethane (**19c**) generates 1-chlorocycloheptatetraene (**26c**): IR (Ar, 15 K) vide supra. Shorter wavelength irradiation (>212 nm) of **26c** produces some phenylchloromethylene (**22c**): IR (Ar, 15 K) vide supra.

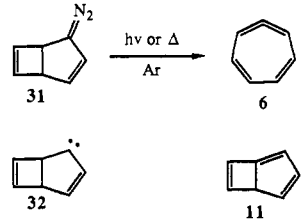
7-Acetoxynorbornadiene (9). Flash vacuum thermolysis (510 °C, 75% conversion) of 7-acetoxynorbornadiene (**9**) followed by cocondensation with argon produces cycloheptatetraene (**6**) (IR (Ar, 15 K) vide supra) and acetic acid (IR (Ar, 15 K) 3558 m, 2705 w, 2650 w, 2590 w, 1775 s, 1240 m, 1185 s, 990 s, 640 s, 538 m cm^{-1}) along with a small amount of fulvenallene (**15**): IR (Ar, 15 K) vide supra. Irradiation (>338 nm) results in no detectable change in the infrared spectrum. This rules out the presence of cycloheptatrienylidene (**5**). Cycloheptatrienylidene is known to disappear under these irradiation conditions.[28] Thermolysis of **9** at 600 °C (100% conversion) gives roughly equal amounts of cycloheptatetraene (**6**) and fulvenallene (**15**), along with some benzene. At 745 °C, **9** produces fulvenallene (**15**), the ethynylcyclopentadienes (**16**) (IR (Ar, 15 K) vide supra), and benzene. The observation of carbon dioxide suggests the onset of acetic acid decomposition. The mechanism of the rearrangement of **9** to **6** will be considered in a separate publication.

Scheme III

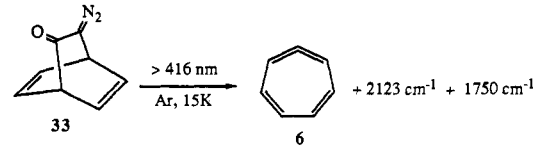




2-Diazobicyclo[3.2.0]hepta-3,6-diene (31). 2-Diazobicyclo[3.2.0]hepta-3,6-diene (**31**) proved to be a surprising precursor to cycloheptatetraene.[38] Irradiation (>574 nm) of argon matrix-isolated **31** generates cycloheptatetraene (**6**): IR (Ar, 15 K) vide supra. Infrared spectroscopy shows that flash vacuum thermolysis of **31** (250 °C, 100% conversion) followed by cocondensation with argon also produces cycloheptatetraene exclusively. We obtained no spectroscopic evidence for carbene **32** or triene **11** in either the thermal or the photochemical experiments.



8-Diazobicyclo[2.2.2]octa-2,5-dien-7-one (33). Irradiation (>416 nm, 3616 min) of argon matrix-isolated diazoketone **33** produces cycloheptatetraene (**6**) (IR (Ar, 15 K) vide supra) and carbon monoxide: IR (Ar, 15 K) 2130 s cm^{-1}. In addition, ketene (2123 cm^{-1}) and carbonyl (1750 cm^{-1}) containing species are observed. Under shorter wavelength irradiation (>320 nm, 175 min), the ketene (2123 cm^{-1}) increases, while the carbonyl (1750 cm^{-1}) disappears. The details of these photochemical rearrangements will be considered in a separate publication.



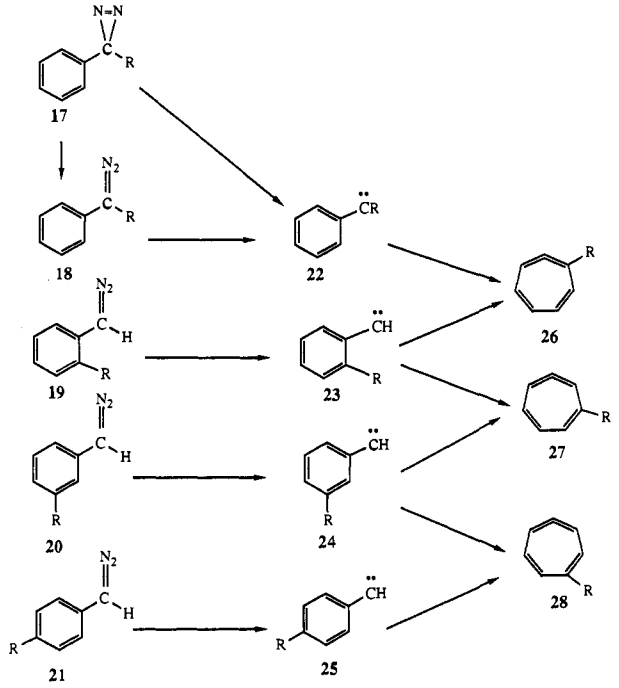
Discussion

1,2,4,6-Cycloheptatetraene Characterization. Our IR and UV results clearly establish that (a) photolysis of phenyldiazirine (**1**), (b) thermolysis or photolysis of phenyldiazomethane (**2**), (c)

(37) The infrared spectrum of phenylchloromethylene has been previously reported: Mal'tsev, A. K.; Zuev, R. P. S.; Nefedov, O. M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1985**, 2159. Ganzer, G. A.; Sheridan, R. S.; Liu, M. T. H. *J. Am. Chem. Soc.* **1986**, *108*, 1517–1520.

(38) Chapman, O. L.; Abelt, C. J. *J. Org. Chem.*, in press. Abelt, C. J. Ph.D. Dissertation, University of California, Los Angeles, CA, 1983.

Scheme IV

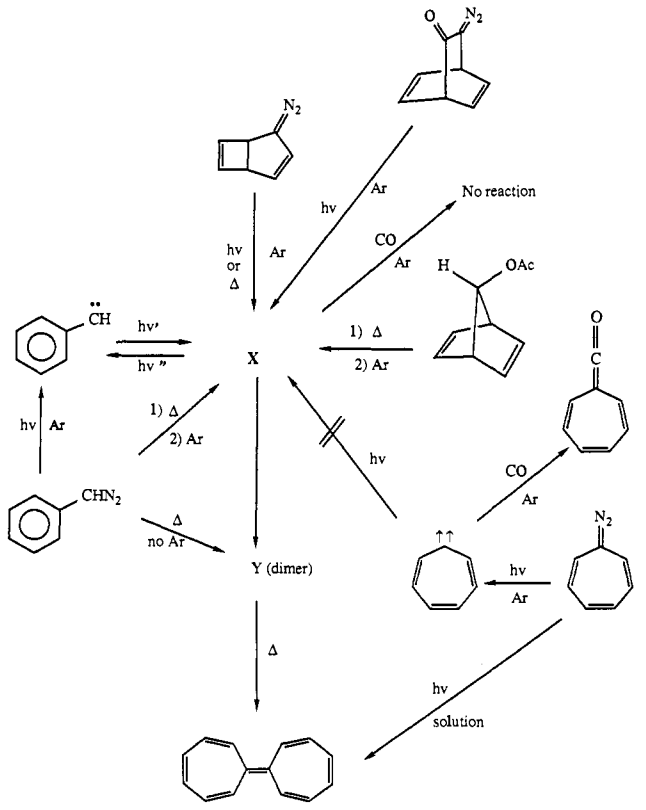


a R = D

b R = F

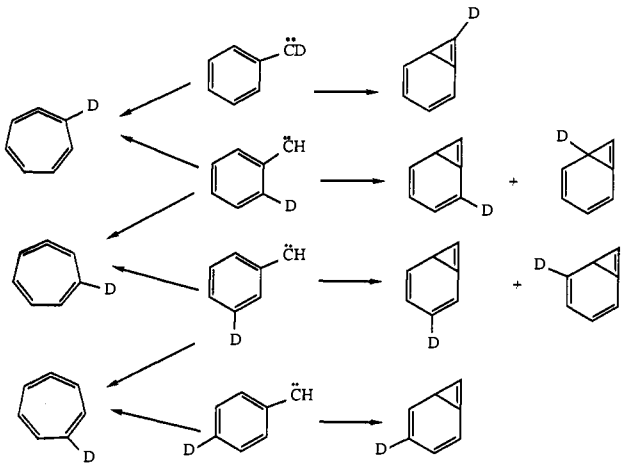
c R = Cl

Scheme V



photolysis of phenylmethylene (**3**), (d) thermolysis or photolysis of 2-diazobicyclo[3.2.0]hepta-3,6-diene (**31**), (e) photolysis of 8-diazobicyclo[2.2.2]octa-2,5-dien-7-one (**33**), and (f) thermolysis of 7-acetoxynorbornadiene (**9**) produce the same species X (Scheme V). Obviously, X is a key intermediate in the chemistry of C_7H_6 isomers. We entertain bicyclo[4.1.0]hepta-2,4,6-triene (**4**), bicyclo[3.2.0]hepta-1,3,6-triene (**11**), cycloheptatrienylidene (**5**), and 1,2,4,6-cycloheptatetraene (**6**) as possible structures for

Scheme VI



X. The following discussion contains the detailed arguments for our conclusion that X = 1,2,4,6-cycloheptatetraene (**6**).

Cycloheptatrienylidene (**5**) is rigorously excluded as the structure for X.[28] The IR and UV spectra of **5** do not match those of X. Cycloheptatrienylidene displays a triplet ESR signal; X does not. Cycloheptatrienylidene rearranges upon irradiation with $\lambda > 514$ nm; X does not. Finally, cycloheptatrienylidene reacts with carbon monoxide to form a ketene; X does not.

Dimerization chemistry rigorously excludes bicyclo[3.2.0]-hepta-1,3,6-triene (**11**) as the structure for X. Compound X and triene **11** produce different dimers. Heptafulvalene (**8**) is the isolable dimer of X at room temperature. In contrast, **11** produces a stable [2 + 2] dimer (**12**).[18,39] **12** does not rearrange to heptafulvalene (**8**) at room temperature.[18,39]

Deuterium labeling studies rigorously exclude bicyclo[4.1.0]-hepta-2,4,6-triene (**4**) as the structure for X. The evidence is based upon the deuterium distribution in the photoproducts of the monodeuterio phenylmethylenes (**22a–25a**). Scheme VI shows the deuteriobicyclo[4.1.0]hepta-2,4,6-triene products expected from a cyclization mechanism and the deuteriocyclohepta-1,2,4,6-tetraene products expected from a ring-expansion mechanism. If the cyclization mechanism operates, then each monodeuterio phenylmethylene produces unique products. If, however, the ring-expansion mechanism operates, then each monodeuterio phenylmethylene produces a product in common with at least one other monodeuterio phenylmethylene. Experimentally, we observe that **22a** produces a product in common with **23a**, **23a** produces one product in common with **22a** and another in common with **24a**, **24a** produces one product in common with **23a** and another in common with **25a**, and **25a** produces a product in common with **24a**. (Figure 4 contains pertinent portions of the infrared spectra of these transformations.) We thus conclude that the label distribution is inconsistent with X = bicyclo[4.1.0]hepta-2,4,6-triene (**4**) but consistent with X = 1,2,4,6-cycloheptatetraene (**6**).

We are able to distinguish between bicyclo[4.1.0]heptatriene (**4**) and cycloheptatetraene (**6**) on the basis of the characteristic infrared absorptions of their respective cyclopropene and allene moieties. Cyclopropenes with substitution patterns similar to that of the cyclopropene moiety of bicyclo[4.1.0]heptatriene exhibit ring vibrational frequencies at 1768 and 1740 cm^{-1}, respectively (Table I). Although ordinary allenes display rather intense infrared stretching frequencies at approximately 1950 cm^{-1} (Table II), cumulene stretching vibrations exhibit large shifts to lower frequencies upon incorporation in a small, strained ring. Wentrup observed the allene stretch of 1,2-cyclohexadiene at 1886 cm^{-1}.[40] The ketenimine stretch of 1-aza-1,2,4,6-cycloheptatetraene (1895

(39) Breslow, R.; Washburn, W.; Bergman, R. G. *J. Am. Chem. Soc.* **1969**, *91*, 196. Breslow, R.; Washburn, W. *J. Am. Chem. Soc.* **1970**, *92*, 427–428. Bauld, N. L.; Dahl, C. E.; Rim, Y. S. *J. Am. Chem. Soc.* **1969**, *91*, 2787–2788.

(40) Wentrup, C.; Gross, G.; Maquestiau, A.; Flammang, R. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 542–543.

Table I. Cyclopropene Infrared Ring Vibrations

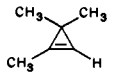
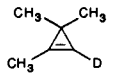
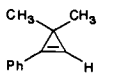
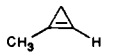
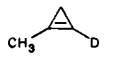
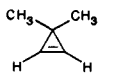
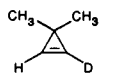
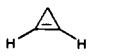
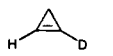
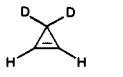
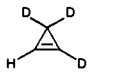
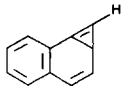
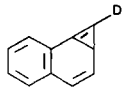
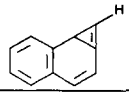
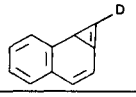
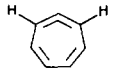
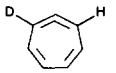
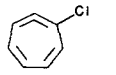
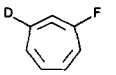
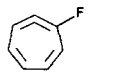
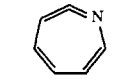
	cm^{-1}	ref		cm^{-1}	ref
	1768	45		1718	45
	1740	45			
	1790, 1787	69		1740, 1737	69
	1632	45		1578	45
	1653	70		1607	70
	1648	70		1593	70
	1765, 1755	25		1720	25
	1755, 1750	25		1715	25

Table II. Allene Infrared Asymmetric Stretching Frequencies

	cm^{-1}	ref		cm^{-1}	ref
$CH_2{=}C{=}CH_2$	1957	46	$CD_2{=}C{=}CH_2$	1941	46
$CH_2{=}C{=}CHF$	1970 m	71			
$CHF{=}C{=}CHF$	1987 vs	71			
$CH_2{=}C{=}CF_2$	2026 s	71	$CHD{=}C{=}CF_2$	2008 s	71
			$CD_2{=}C{=}CF_2$	1990 s	71
$CHF{=}C{=}CF_2$	2038 s	71			
$CF_2{=}C{=}CF_2$	2052 s	71			
$CH_2{=}C{=}CHCl$	1963 m	72			
$CH_2{=}C{=}CHBr$	1961 w	72			
$CH_2{=}C{=}CHI$	1953 m	72			
	1824 w	*a*		1820 w	*a*
	1816 w	*a*		1811 w	*a*
	1810 m	*a*		1799 m	*a*
	1809 m	*a*			

[a] This work.

cm^{-1}) appears ca. 105 cm^{-1} lower than an unstrained, acyclic ketenimine.[8a] Most importantly, 1-aza-1,3,4,6-cycloheptatetraene, the common photoproduct derived from matrix-isolated 3-pyridylmethylene and 4-pyridylmethylene, exhibits an infrared absorption at 1810 cm^{-1}.[41]



$\nu_{C=C=N}$ = 1895 cm^{-1}

$\nu_{C=C=C}$ = 1810 cm^{-1}

Close examination of the region between 2000 and 1700 cm^{-1} of the infrared spectra of X, as generated from various precursors, reveals weak bands at 1824 and 1816 cm^{-1}. With phenyldiazomethane or phenylmethylene precursors, we observe an additional band at 1760 cm^{-1}. The intensity of the 1760-cm^{-1} absorption varied considerably (relative to the C–H deformation modes) from experiment to experiment. The band proved to be an artifact whose intensity was inversely proportional to the rigor with which oxygen was excluded from the matrix and/or sample.[42] The intensity of the doublet appearing at 1824 and 1816 cm^{-1} did not vary relative to the C–H deformation modes. These bands clearly pertain to X. The 1824- and 1816-cm^{-1} bands appear 40–70 cm^{-1} higher in frequency than expected for a bicyclo[4.1.0]hepta-

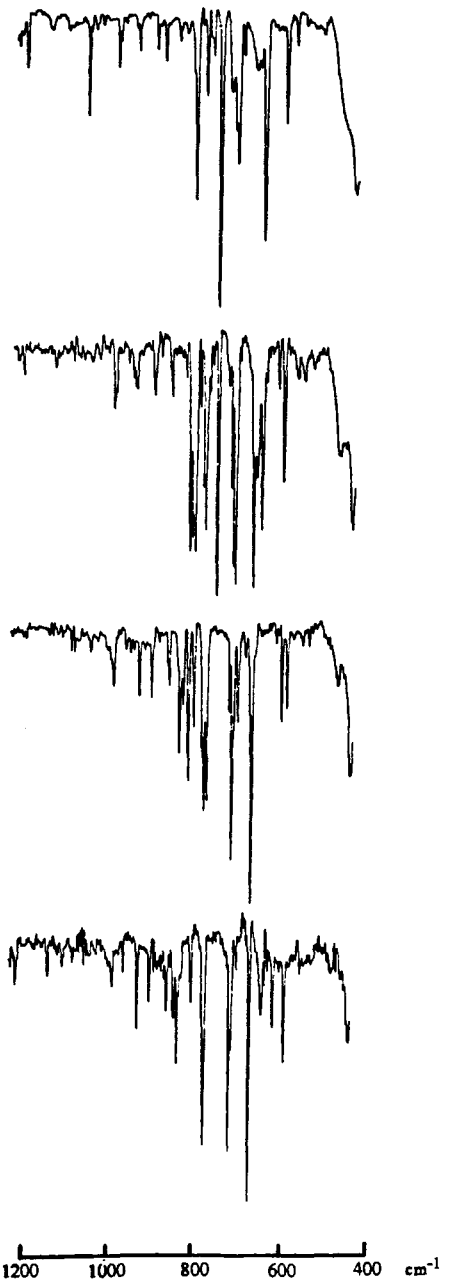


Figure 4. Top: Infrared spectrum of 1-deuteriocycloheptatetraene (**26a**) formed upon irradiation (>364 nm, 122 min) of α-deuteriophenylmethylene (**22a**) matrix isolated in argon at 15 K. Middle/top: Infrared spectrum of a mixture of 1-deuterio- and 4-deuteriocycloheptatetraene (**26a** and **27a**) formed upon irradiation (>416 nm, 338 min) of *o*-deuteriophenylmethylene (**23a**) matrix isolated in argon at 15 K. Middle/bottom: Infrared spectrum of a mixture of 4-deuterio- and 5-deuteriocycloheptatetraene (**27a** and **28a**) formed upon irradiation (>416 nm, 921 min) of *m*-deuteriophenylmethylene (**24a**) matrix isolated in argon at 15 K. Bottom: Infrared spectrum of 5-deuteriocycloheptatetraene (**28a**) formed upon irradiation (>416 nm, 182 min) of *p*-deuteriophenylmethylene (**25a**) matrix isolated in argon at 15 K.

(41) Chapman, O. L.; Sheridan, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 3690–3692.

(42) Reaction of phenylmethylene with O_2 in low-temperature matrices produces benzaldehyde (1720 cm^{-1}) and benzoic acid (1760 cm^{-1}).[43] Gasser estimated that a monolayer of atmospheric constituents condenses every 2 s at the pressures (10^{-6} torr) used in the matrix-isolation experiments.[44] Therefore, some oxygen contamination is inevitable, particularly during 2–3-day photolyses. (First-row diatomics are small enough to diffuse through solid argon.)

(43) Sander, W. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 988–989.

(44) Gasser, R. P. H. *Q. Rev., Chem. Soc.* **1971**, *25*, 223–238.

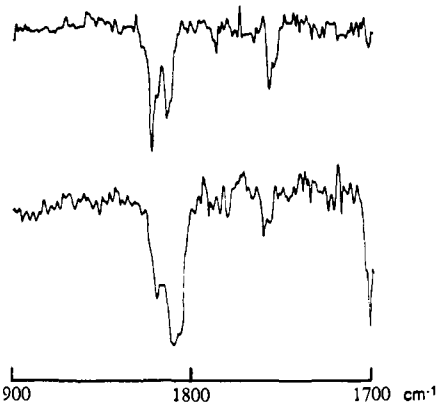


Figure 5. Top: Infrared spectrum of cycloheptatetraene (6) formed upon irradiation (>416 nm, 95 min; >364 nm, 108 min) of phenylmethylene (**3**) matrix isolated in argon at 15 K. Bottom: Infrared spectrum of 1-deuteriocycloheptatetraene (**26a**) formed upon irradiation (>364 nm, 122 min) of α-deuteriophenylmethylene (**22a**) matrix isolated in argon at 15 K.

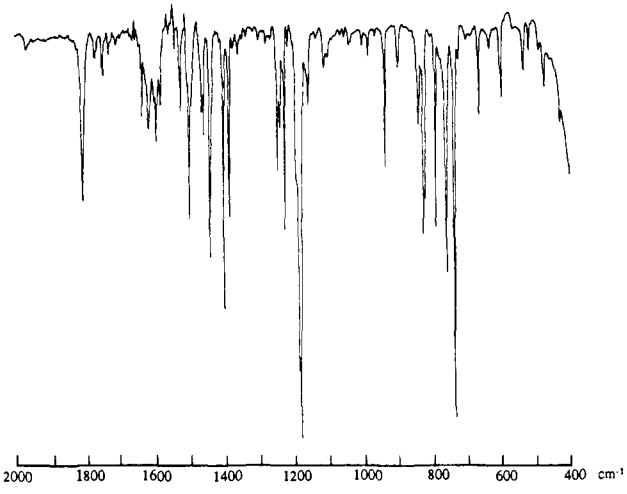


Figure 6. Infrared spectrum of 1-fluorocycloheptatetraene (**26b**) formed upon irradiation (>416 nm, 990 min) of *o*-fluorophenyldiazomethane (**19b**) matrix isolated in argon at 15 K.

2,4,6-triene (**4**) intermediate. Our recent study of the photochemistry of the 1-naphthyl- and 2-naphthyldiazomethanes led to the characterization of 4,5-benzobicyclo[4.1.0]hepta-2,4,6-triene (1765, 1755 cm^{-1}) and 2,3-benzobicyclo[4.1.0]hepta-2,4,6-triene (1755, 1750 cm^{-1}) (Table I).[25] The excellent agreement of the infrared spectra of the benzobicyclo[4.1.0]hepta-2,4,6-trienes with that predicted by our model compounds casts serious doubt on whether the 1824- and 1816-cm^{-1} bands can be assigned to the parent bicyclo[4.1.0]hepta-2,4,6-triene (**4**).

We confirmed our infrared assignment by studying several substituted derivatives of X. Substitution of a vinylic hydrogen by deuterium lowers the cyclopropene ring vibrational frequency by 40–50 cm^{-1}.[45] This apparently results from the strong coupling of the cyclopropene ring vibrations with the exocyclic vinylic bonds. The magnitude of the frequency shift is not solvent dependent and hence is applicable to the study of matrix-isolated molecules. Table I contains several examples of this effect. In contrast to the large shifts noted for cyclopropenes, deuterium substitution produces considerably smaller changes in allenic stretching frequencies. For example, the asymmetric stretching mode of 1,1-dideuterioallene (1941 cm^{-1}) appears only 16 cm^{-1} lower than that of allene (1957 cm^{-1}) (Table II).[46] Irradiation (>416 nm) of α-deuteriophenylmethylene (**22a**) produces a species exhibiting infrared bands at 1820 and 1810 cm^{-1} (Figure 5). This shift agrees with the behavior expected of 1-deuteriocycloheptatetraene. It is inconsistent with the 7-deuteriobicyclo[4.1.0]heptatriene intermediate and is in strking contrast to the shifts observed upon deuteriation of the 2,3- and 4,5-benzobicyclo[4.1.0]hepta-2,4,6-trienes (Table I).

We find that halogen substitution is also a useful structure probe. Fluorine substitution substantially enhances the intensity of allene absorptions, while producing only slight shifts in the absorption frequency (Table II). Chlorine substitution produces similar, but less pronounced, effects. Photolysis or thermolysis of either the α-halophenylmethylenes (**22b,c**) or the *o*-halophenylmethylenes (**23b,c**) generates new species exhibiting intense absorptions near 1810 cm^{-1} (Figure 6, Table II). These positions and intensities are consistent with the behavior expected for 1-halocyclohepta-1,2,4,6-tetraene structures (**26b,c**). Furthermore, photolysis of the doubly substituted compound, α-deuterio-*o*-fluorophenyldiazomethane (**29**), produces an intense absorption near 1799 cm^{-1}. We attribute the 10-cm^{-1} shift to lower frequency (relative to **26b**) to the isotope shift expected for 3-deuterio-1-fluorocyclohepta-1,2,4,6-tetraene (**30**) (Table II).

29 **30**

Two chemical reactivity studies bear on the cycloheptatetraene assignment. First, X fails to react with carbon monoxide in a CO-doped argon matrix. This result enables us to rule out a carbene structure (e.g., cycloheptatrienylidene (**5**)) for the intermediate (vide supra).[28]

The second reactivity study concerns the dimerization chemistry of X. Generation of X either thermally (370 °C) or photochemically (>416 nm) from phenyldiazomethane, followed by decomposition of the argon matrix, produces heptafulvalene. Stilbene formation in the photochemical process is believed to be due to decomposition of residual phenyldiazomethane. Stilbene is not a dimerization product of X. The flash vacuum thermolysis experiment carried out in the *absence* of argon does not produce X at 10 K. This implies that X is kinetically unstable toward dimerization. The dimerization product (Y) exhibits an infrared spectrum similar to that of heptafulvalene and produces heptafulvalene on warming to room temperature (Figures 2 and 3). The identity of heptafulvalene was established by comparison of IR, UV, ^1H NMR, and capillary GC retention time data with those of the freshly prepared authentic material.[11]

We suggest that the initial product (Y) is the cyclobutane adduct **7** expected upon [2 + 2] dimerization across the strained allene in cycloheptatetraene (**6**). Warming **7** produces heptafulvalene (**8**) by thermal, electrocyclic ring opening. The IR spectra of **7** and **8** are expected to be similar (Figure 2), but the UV–vis spectra differ. The through-conjugated dimer (**7**) absorbs at a longer wavelength than the cross-conjugated heptafulvalene (**8**) (Figure 3). We do not believe that the initial product (Y) is simply a different crystalline form of heptafulvalene. Although Y and **8** display similar IR spectra, the UV–vis spectra exhibit strongly differing absorption maxima (455 vs. 370 nm, respectively). This relatively large difference is difficult to explain solely on the basis of a crystalline-phase change/annealling argument. Vapor-phase deposition of an authentic sample of heptafulvalene onto a cold window at 10 K (neat) gives an infrared spectrum identical with that obtained at room temperature. Thus, heptafulvalene does not crystallize in a different crystalline form at 10 K.

We reported earlier that cycloheptatetraene (**6**) produces a dimer (*m/z* 180) upon warming to room temperature.[26] We were forced to rule out heptafulvalene (**8**) formation, on the basis of comparison of the mass spectral fragmentation pattern of the dimer with the known fragmentation pattern of heptafulvalene.[11] However, we now know that the dimer sample was impure, rendering conclusions based on fragmentation patterns invalid. Our new dimerization studies clearly and unequivocally establish that heptafulvalene (**8**) is the isolable dimer of cycloheptatetraene (**6**) at room temperature. This brings our understanding of cyclo-

(45) Closs, G. L. *Adv. Alicyclic Chem.* **1966**, *1*, 53–127.
(46) Evans, J. C.; Wilmhurst, J. K.; Bernstein, H. J. *Can. J. Chem.* **1956**, *34*, 1139–1142.

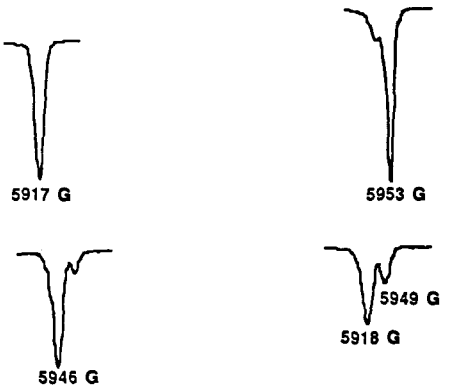


Figure 7. Top left: The Y_2 transition of the ESR spectrum of *p*-deuteriophenylmethylene (**25a**) formed upon irradiation (>478 nm, 2505 min) of *p*-deuteriophenyldiazomethane (**21a**) matrix isolated in argon at 15 K. Bottom left: ESR spectrum showing the appearance of the Y_2 transition of α-deuteriophenylmethylene and the disappearance of the Y_2 transition of *p*-deuteriophenylmethylene upon irradiation (>278 nm, 3750 min) of the sample shown above. Top right: The Y_2 transition of the ESR spectrum of α-deuteriophenylmethylene formed upon irradiation (>478 nm, 1313 min) of α-deuteriophenyldiazomethane (**18a**) matrix isolated in argon at 15 K. Bottom right: ESR spectrum showing the appearance of the Y_2 transition of ring-labeled deuteriophenylmethylenes and the decrease of the Y_2 transition of α-deuteriophenylmethylene upon irradiation (>278 nm, 2495 min) of the sample shown above.

heptatetraene chemistry into accord with the wealth of chemical information on phenyldiazomethane and tropone tosylhydrazone thermolysis and photolysis.[2]

Mechanism of Ring Expansion. Having established that X = 1,2,4,6-cycloheptatetraene, we now consider the mechanism of cycloheptatetraene formation from phenylmethylene (**3**). Does the ring expansion occur directly or does it occur via an undetected bicyclo[4.1.0]hepta-2,4,6-triene (**4**) intermediate? Billups demonstrated that 1-methylbicyclo[4.1.0]hepta-2,4,6-triene thermally rearranges to *o*-tolylmethylene in solution.[15] He did not find any evidence for ring-expanded products, but his conclusion is equivocal because of the poor mass balance of the reaction. Both calculations and experimental evidence led Wentrup to suggest that ring expansion of phenylmethylene (**3**) may occur directly.[14] Although not rigorously demanding, our results also suggest that the reaction occurs directly. We expect **4**, if formed, to be stable to our reaction conditions. We do not expect **4** to absorb light with wavelengths > 416 nm (the irradiation conditions required to induce photochemical rearrangement of **3**), nor do we expect **4** to undergo thermal isomerization at 10 K. Our earlier observation of the analogous benzobicyclo[4.1.0]hepta-2,4,6-trienes[25] establishes our ability to characterize such species. Our failure to observe **4** therefore argues against its formation. Our evidence does not address the possible intermediacy of **4** in the thermal rearrangement pathway.

Arylmethylene Interconversions. In addition to establishing 1,2,4,6-cycloheptatetraene as the thermal and photochemical ring-expansion product of phenylmethylene, our studies also demonstrate the thermal and photochemical reversibility of the ring-expansion reaction. This forms the basis for understanding the mechanism of arylmethylene interconversions. Flash vacuum thermolysis (500 °C, 100% conversion) of phenyldiazomethane (**2**) followed by cocondensation with argon on the tip of our ESR cryostat produces no triplet ESR signal.[33a] This indicates that only a vanishingly small concentration of phenylmethylene (**3**) can exist in equilibrium with cycloheptatetraene (**6**) in the gas phase at 500 °C. Irradiation of the matrix-isolated cycloheptatetraene (**6**) (>279 nm) generates a small, steady-state concentration of triplet phenylmethylene (**2**), thereby establishing the photochemical reversibility of the ring-expansion process.[34] The thermal reversibility is not established directly by any work described here but has been established by others.[2,12]

Deuterium substitution in the *o*-, *m*-, and *p*-deuteriophenylmethylenes does not perturb the triplet ESR signals enough to distinguish between the isomers. However, the position of the Y_2 transition clearly distinguishes the α-isomer (**22a**) from the ring-labeled isomers. We therefore conclude with certainty that irradiation (>278 nm) of α-deuteriophenylmethylene results in equilibration with the ring-labeled isomers and that irradiation (>278 nm) of each of the three ring-labeled isomers results in equilibration with the α-isomer (Figure 7). The deuteriophenylmethylene equilibrations occur via deuteriocycloheptatetraene intermediates, on the basis of the species observed by infrared spectroscopy. Irradiation (>278 nm) of 5-deuteriocycloheptatetraene (**28a**), generated from *p*-deuteriophenylmethylene, results in equilibration first with 4-deuteriocycloheptatetraene (**27a**) and then with 1-deuteriocycloheptatetraene (**26a**). Figure 8 shows how the deuteriocycloheptatetraene concentrations evolve during the photolysis. Similarly, irradiation (>278 nm) of the mixture of 1- and 4-deuteriocycloheptatetraenes obtained from *o*-deuteriophenylmethylene produces 5-deuteriocycloheptatetraene, and irradiation (>278 nm) of the mixture of 4- and 5-deuteriocycloheptatetraenes obtained from *m*-deuteriophenylmethylene produces 1-deuteriocycloheptatetraene. The sequential isomerization of the deuteriocycloheptatetraenes is consistent with the linear rearrangement mechanism depicted in Scheme IV.

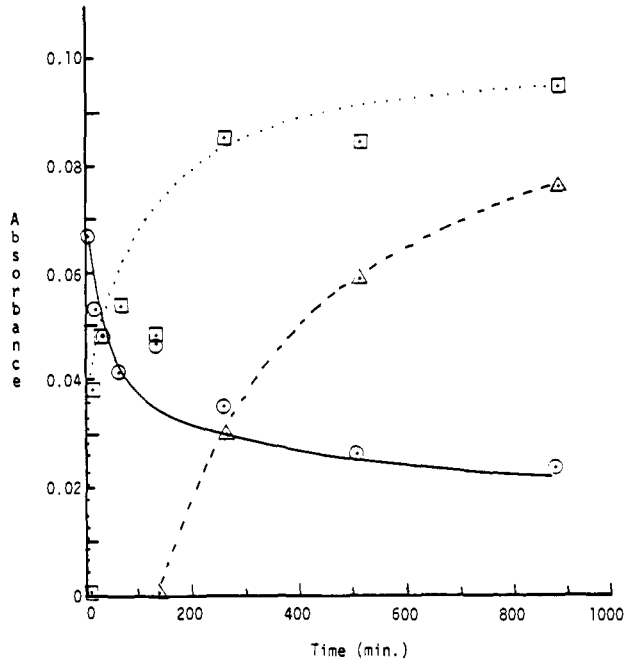


Figure 8. Plot of time dependence of selected bands due to 1-deuteriocycloheptatetraene (724 cm^{-1}, represented by △), 4-deuteriocycloheptatetraene (787 cm^{-1}, represented by □), and 5-deuteriocycloheptatetraene (584 cm^{-1}, represented by ○), on irradiation (λ > 278 nm) of matrix-isolated 5-deuteriocycloheptatetraene.

Flash vacuum thermolysis (500 °C, 100% conversion) of *p*-deuteriophenyldiazomethane followed by cocondensation with argon produces a 1:1:1 mixture of 1-, 4-, and 5-deuteriocycloheptatetraenes, as observed by infrared spectroscopy. On the basis of the mechanism in Scheme IV, both 1- and 4-deuteriocycloheptatetraene form via multiple ring-expansion/ring-contraction steps.[47] This implies the thermal reversibility of the ring-expansion process. Flash vacuum thermolysis (500 °C, 100% conversion) of each of the isomeric deuteriophenyldiazomethanes followed by cocondensation with argon on the tip of our ESR cryostat produces a mixture of deuteriocycloheptatetraenes. No triplet ESR signal is observed.[33b] Irradiation (>278 nm) of the sample rapidly generates the ESR spectra of both α-deuteriophenylmethylene

(47) Multiple rearrangements occur during the gas-phase thermolyses of the tolylmethylenes[2,4,13,48,49] and the naphthylmethylenes.[50]

(48) Chapman, O. L.; McMahon, R. J.; West, P. R. *J. Am. Chem. Soc.* **1984**, *106*, 7973–7974.
(49) Trahanovsky, W. S.; Schribner, M. E. *J. Am. Chem. Soc.* **1984**, *106*, 7976–7978.
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and the ring-labeled isomers.[34] This once again establishes the photochemical reversibility of the ring-expansion process.

Infrared spectroscopy clearly establishes the thermal and photochemical interconversions of the *o*-halophenylmethylenes with the α-halophenylmethylenes via the 1-halocycloheptatetraenes.[51] The significance of these observations lies in the fact that the α-halophenylmethylenes are ground-state singlet carbenes. This is the first report of ring expansion by singlet arylcarbenes. The detailed characterization of the halo-substituted intermediates and discussion of their chemistry will be presented in a separate full paper.[52]

High-Temperature Rearrangements. We briefly note that thermolysis (755 °C) of phenyldiazomethane (**2**) produces only fulvenallene (**15**) and the isomeric ethynylcyclopentadienes (**16**). Ring contraction of **3** at high temperatures has long been established, but the mechanism of the reaction remains unclear.[2] In addition, thermolysis (510–745 °C) of 7-acetoxynorbornadiene (**9**) also produces **15** and **16**. This was expected, because **2** and **9** produce a common intermediate (cycloheptatetraene (**6**)) at lower temperatures (≤500 °C). The ratio of fulvenallene (**15**) to ethynylcyclopentadienes (**16**) changes with temperature. Relatively more **16** forms at higher temperatures. This observation is consistent with Wentrup's conclusion that fulvenallene (**15**) is the first-formed product, which subsequently isomerizes to the ethynylcyclopentadienes (**16**).[2]

Summary of Evidence for 1,2,4,6-Cycloheptatetraene. (1) Infrared spectroscopy reveals an allene stretch at 1824 and 1816 cm^{-1}. (2) Halogen substitution (X = F, Cl) substantially enhances the intensity of the allene stretch. (3) The isotope shift of infrared bands upon deuteriation is consistent with an allene but rules out bicyclo[4.1.0]hepta-2,4,6-triene (**4**). (4) Deuterium labeling rigorously excludes bicyclo[4.1.0]hepta-2,4,6-triene (**4**). (5) Observation of the labile [2 + 2] dimer (**7**) that opens to heptafulvalene (**8**) rigorously excludes bicyclo[3.2.0]hepta-1,3,6-triene (**11**). (6) Comparison of chemical and spectroscopic properties rigorously excludes cycloheptatrienylidene (**5**). (7) Theoretical calculations place cycloheptatetraene (**6**) 16–48 kcal/mol below cycloheptatrienylidene (**5**) in energy.

Experimental Section

^1H NMR spectra were recorded on Varian T-60 or Bruker WP-200 instruments. ^{13}C NMR spectra were recorded on a Bruker WP-200 instrument. Chemical shifts (δ) are reported as ppm downfield from internal $SiMe_4$. Melting points were determined on a Thomas-Hoover Unimelt apparatus in open capillaries and are uncorrected. Elemental analyses were performed by Spang Microanalytical Laboratory (Eagle Harbor, MI). Mass spectra were obtained on AEI MS-9 or MS-902 spectrometers.

Capillary gas chromatography utilized a Hewlett-Packard Model 5710A equipped with a fused silica column (0.25-mm i.d. × 30 m, 0.25-μm loading DB-5). GC–mass spectra were obtained on a Kratos MS25 spectrometer equipped with a similar capillary column.

Infrared spectroscopy was performed with a Beckman 4250, a Perkin-Elmer 580B with Model 3600 data station, or a Nicolet 60SX spectrometer. Ultraviolet–visible spectroscopy was performed with a Perkin-Elmer 330 with Model 3600 data station. ESR spectra were obtained with an X-band spectrometer constructed from a variety of commercial components. The magnetic field was calibrated with an NMR gaussmeter, and the microwave frequency was determined by the use of a DPPH reference. The best fit of the observed ESR spectra with the spin Hamiltonian[53] (assuming $g_x = g_y = g_z = g_e$) provided the zero-field splitting parameters.

Matrix Isolation Spectroscopy. The apparatus and experimental technique used for the study of matrix-isolated reactive species have been described elsewhere.[54] In the dimerization studies, the sample window containing the argon matrix is warmed to ca. 40 K by using the temperature controller. The argon is allowed to sublime away over 15 min. Occasionally a piece of the matrix falls off the window into the bottom of the inner shroud, but careful warming minimizes problems associated with sample spattering throughout the inside of the apparatus. The Displex is then turned off, the window temperature is raised to 300 K, and a small amount of argon gas is admitted to facilitate the warmup process. In the early stages of the warming, when the window is at 300 K and the inner shroud is at ca. 40 K, most of the sample distills from the window to the bottom of the inner shroud. When the entire system has reached room temperature, the apparatus is disassembled. The sample is rinsed off the window and the inner shroud with $CDCl_3$ (100% D; Aldrich).

General Procedure for Tosylhydrazone Preparation. In a typical preparation, 1.0 equiv of aromatic aldehyde is added to a magnetically stirred slurry of 1.0 equiv of *p*-toluenesulfonhydrazide (Aldrich, recrystallized from water) in absolute ethanol. The solution becomes homogeneous within minutes. The tosylhydrazone precipitates upon stirring a few hours at room temperature. The product is collected by suction filtration, washed with petroleum ether, and recrystallized from absolute ethanol or chloroform/heptane.

General Procedure for Tosylhydrazone Sodium Salt Preparation.[55] In a typical preparation, 0.15 g of tosylhydrazone is dissolved in 20 mL of CH_2Cl_2 and treated with 1.0 equiv of NaH/oil. After stirring for 1–2 h, a viscous, white solution is obtained. Petroleum ether (25 mL) is added, and the gummy white tosylhydrazone sodium salt is collected by suction filtration. The salt is dried in vacuo overnight and crushed to a fine powder with a spatula (yield = 95–100%).

General Procedure for Diazo Compound Preparation.[55] The freshly prepared salt (ca. 0.15 g) is placed in a 25-mL, pear-shaped flask. An adapter permits the diazo compound to distill from the flask directly into the tube used to sublime the sample onto the matrix isolation sample window. The apparatus is evacuated to 0.10 torr and heated to 40–50 °C for 15–30 min with a Kugelrohr oven. The temperature is then raised to ca. 90 °C, and a dry ice bath is placed around the receiver. The deeply colored diazo compound condenses in the sample tube over 45 min. The apparatus is vented with dry N_2, and the sample is subjected to three freeze–pump–thaw cycles at its appropriate deposition temperature. The sample tube is again vented with dry N_2 and attached to the matrix isolation apparatus. After the residual pressure drops below 1×10^{-5} torr, the diazo compound is suitable for matrix isolation without requiring any further purification.

General Procedure for Preparation of α-Deuterio Derivatives. The carboxylic acid corresponding to the desired deuterioaldehyde is treated with MeOH/HCl to produce the methyl ester. The ester is reduced to the α,α-dideuterioarylmethanol with $LiAlD_4$ in Et_2O. Oxidation of the arylmethanol with ceric ammonium nitrate in H_2O affords the α-deuterioaldehyde.[56] The tosylhydrazone is then prepared as described above. However, before the salt is prepared, the N–H proton must be exchanged for N–D. The deuteriotosylhydrazone is dissolved in CH_3CN and treated with D_2O. The solvent is evaporated, and the residual D_2O is azeotropically removed with several portions of CH_3CN. The sodium salt is then prepared from the dideuteriotosylhydrazone in the usual manner. If the D_2O exchange step is omitted, the isotopic purity in the α-deuterioaryldiazomethane drops, due to scrambling in the salt formation step.

General Procedure for the Preparation of Ring-Deuteriated Benzaldehydes. The appropriate bromotoluene (Aldrich) in 25 mL of anhydrous ether is added to 1.1 equiv of magnesium turnings in 20 mL of anhydrous ether at such a rate as to maintain a reflux (ca. 30 min). The reaction mixture is then refluxed another 30 min. After the mixture is cooled, the Grignard reagent is treated dropwise with 8 mL of deuterium oxide and stirred overnight. The resulting suspension is filtered and distilled to afford the deuteriotoluene.[57]

The deuteriotoluene is added to a suspension of 1.2 equiv of *N*-bromosuccinimide in 30 mL of benzene.[57] Benzoyl peroxide (ca. 50 mg) is added, and the resulting mixture is heated to reflux while being irradiated with a G.E. Sunlamp. After 30 min, the suspension is cooled and filtered with the aid of 40 mL of chloroform. Forty milliliters of the solvent is removed by distillation, and then a solution of 1.2 equiv of hexamethylenetetraamine in 17 mL of acetic acid and 10 mL of water is added to the reaction mixture. Distillation is resumed and continued until the temperature rises above 90 °C, whereupon the mixture is re-

(51) The *o*-halophenylmethylenes (**23b,c**) ring-expand in only one of the two possible directions available to them. The 4-halocycloheptatetraenes (**27b,c**) are not produced. The exclusive ring expansion of 2-substituted arylcarbenes to 1-substituted cycloheptatetraenes has also been observed in the cases of *o*-tolylmethylene,[48] 2-methyl-5-(trideuteriomethyl)phenylmethylene,[49] and 2-pyridylmethylene.[8a,27]

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fluxed for 2 h. Concentrated hydrochloric acid (6 mL) is then added, and the solution is refluxed for an additional 15 min. After the mixture is cooled and diluted with 75 mL of water, it is neutralized with sodium carbonate and extracted with ether. The ether extracts are washed with 1 N sodium hydroxide and water, dried over $MgSO_4$, and evaporated to afford the crude deuteriobenzaldehyde.

Heptafulvalene (8). An authentic sample of heptafulvalene was prepared by the method of Jones and Ennis:[11] IR (Ar, 15 K) 3019 m, 2924 s, 2850 m, 1559 m, 1540 m, 1452 m, 1382 w, 932 w, 892 w, 796 m, 785 w, 711 s, 475 s, 402 w cm^{-1}; UV (EtOH) λ_{max} (log ϵ) 358 (4.33), 231 nm (4.39); ^1H NMR (200 MHz, $CDCl_3$) δ 5.86 (br s, 8 H), 5.99 (br s, 4 H), the resonances are not well resolved; mass spectrum (70 eV), *m/z* (relative intensity) 180 (M^+, 100), 165 (44), 153 (39), 139 (6), 115 (46), 102 (11), 90 (8), 89 (24), 76 (20), 63 (27).

Benzaldehyde Tosylhydrazone. Prepared from benzaldehyde (Baker) in 84% yield: mp 127–128 °C [lit.[58] mp 127–128 °C]; ^1H NMR ($CDCl_3$) δ 2.33 (s, 3 H), 7.17–8.00 (m, 10 H), 8.53 (s, 1 H); mass spectrum (16 eV), *m/z* (relative intensity) 174 (M^+, 61), 119 (44), 118 (84), 92 (21), 91 (13), 90 (100); Anal. ($C_{14}H_{14}N_2O_2S$): C, H, N.

Phenyldiazomethane (2): IR (Ar, 15 K), 3195 w, 3080 w, 3030 w, 2055 s, 1600 m, 1497 m, 1385 m, 1332 w, 1299 w, 1205 w, 1182 w, 1072 w, 886 w, 743 s, 687 m, 640 m, 440 m cm^{-1}; UV (Ar, 10 K) λ_{max} 307, 300, 295, 274, 229, 216, 213 nm; ^1H NMR (CCl_4) δ 4.83 (s, 1 H), 6.73–7.50 (m, 5 H). The deep-red diazo compound was sublimed at −41 °C (10^{-6} torr) and codeposited with argon to form a matrix.

α-Deuteriobenzaldehyde Tosylhydrazone. Prepared from α-deuteriobenzaldehyde in 65% yield: mp 127–128 °C; ^1H NMR ($D_2O/CDCl_3$) δ 2.37 (s, 3 H), 7.17–8.00 (m, 9 H), 8.71 (s, 1 H); mass spectrum (16 eV), *m/z* (relative intensity) 275 (M^+, 2.7), 139 (35), 124 (10), 119 (43), 92 (37), 91 (100), 90 (20), 274 not detected.

α-Deuteriophenyldiazomethane (18a): IR (Ar, 15 K) 3208 w, 3080 w, 3040 w, 2105 w, 2065 s, 1612 w, 1602 m, 1503 m, 1488 w, 1456 w, 1351 m, 1331 w, 1267 w, 1181 w, 1077 w, 1032 w, 890 w, 749 s, 691 m, 633 m, 470 w, 370 w cm^{-1}; ^1H NMR (CCl_4) δ 6.78–7.45 (m). The deep-red diazo compound was sublimed at −41 °C (10^{-6} torr) and codeposited with argon to form a matrix.

***o*-Deuteriotoluene.** *o*-Bromotoluene (24 g, 140 mmol) afforded *o*-deuteriotoluene (5.46 g, 59 mmol) in 42% yield: ^1H NMR (neat) δ 2.12 (s, 3 H), 7.04 (br s, 4 H).

***o*-Deuteriobenzaldehyde.** *o*-Deuteriotoluene (5.46 g, 59 mmol) produced *o*-deuteriobenzaldehyde (4.45 g, 42 mmol) in 70% yield: ^1H NMR (CCl_4) δ 7.38–7.93 (m, 4 H), 9.92 (s, 1 H).

***o*-Deuteriobenzaldehyde Tosylhydrazone.** Prepared from *o*-deuteriobenzaldehyde in 56% yield: mp 126–127 °C; ^1H NMR ($CDCl_3$) δ 2.38 (s, 3 H), 7.17–7.90 (m. 9 H), 8.50 (s, 1 H); mass spectrum (16 eV), *m/z* (relative intensity) 275 (M^+, 3.8), 274 (0.6), 139 (33), 124 (5), 120 (11), 119 (44), 118 (12), 92 (51), 91 (100), 90 (34).

***o*-Deuteriophenyldiazomethane (19a):** IR (Ar, 15 K) 3200 w, 3109 w, 3093 w, 3079 m, 3025 w, 2060 s, 1595 s, 1574 m, 1499 w, 1482 s, 1478 s, 1451 m, 1388 s, 1380 m, 1210 m, 946 w, 761 s, 742 s, 689 m, 640 s, 625 s, 437 s cm^{-1}. The deep-red diazo compound was sublimed at −41 °C (10^{-6} torr) and codeposited with argon to form a matrix.

***m*-Deuteriotoluene.** *m*-Bromotoluene (22.5 g, 132 mmol) afforded *m*-deuteriotoluene (8.0 g, 86 mmol) in 65% yield: ^1H NMR (neat) δ 2.15 (s, 3 H), 6.83–7.17 (m, 4 H).

***m*-Deuteriobenzaldehyde.** *m*-Deuteriotoluene (8.0 g, 86 mmol) produced *m*-deuteriobenzaldehyde (7.91 g, 74 mmol) in 86% yield: ^1H NMR (CCl_4) δ 7.38–7.63 (m, 2 H), 7.70–7.90 (m, 2 H), 9.93 (s, 1 H); mass spectrum (16 eV), *m/z* (relative intensity) 108 (13.9), 107 (M^+, 100), 106 (71).

***m*-Deuteriobenzaldehyde Tosylhydrazone.** Prepared from *m*-deuteriobenzaldehyde in 60% yield: mp 127–127.5 °C; ^1H NMR ($CDCl_3$) δ 2.45 (s, 3 H), 7.15–7.95 (m, 9 H), 8.48 (s, 1 H); mass spectrum (16 eV), *m/z* (relative intensity) 275 (M^+, 12.2), 274 (1.4), 139 (4.7), 120 (32), 119 (68), 92 (36), 91 (100), 90 (15).

***m*-Deuteriophenyldiazomethane (20a):** IR (Ar, 15 K) 3205 w, 3105 w, 3093 w, 3070 w, 3013 w, 2060 s, 1596 s, 1483 s, 1443 m, 1388 s, 1382 s, 1369 s, 1202 m, 986 m, 795 s, 744 w, 690 m, 666 s, 640 s, 632 s, 432 m cm^{-1}. The deep-red diazo compound was sublimed at −41 °C (10^{-6} torr) and codeposited with argon to form a matrix.

***p*-Deuteriotoluene.** *p*-Bromotoluene (20.25 g, 118 mmol) afforded *p*-deuteriotoluene (6.27 g, 67 mmol) in 57% yield: ^1H NMR (neat) δ 1.57 (s, 3 H), 6.33–6.67 (m, 4 H).

***p*-Deuteriobenzaldehyde.** *p*-Deuteriotoluene (6.27 g, 67 mmol) produced *p*-deuteriobenzaldehyde (2.61 g, 24.4 mmol) in 36% yield: ^1H NMR (CCl_4) δ 7.37–7.60 (m, 2 H), 7.72–7.93 (m, 2 H), 9.97 (s, 1 H).

***p*-Deuteriobenzaldehyde Tosylhydrazone.** Prepared from *p*-deuteriobenzaldehyde in 72% yield: mp 127–127.5 °C; ^1H NMR ($CDCl_3$) δ 2.37 (s, 3 H), 7.12–7.90 (m, 9 H), 8.50 (s, 1 H); mass spectrum (16 eV), *m/z* (relative intensity) 275 (M^+, 5.8), 139 (73), 124 (55), 123 (15), 119 (27), 108 (13), 107 (17), 106 (12), 92 (48), 91 (100), 274 not detected.

***p*-Deuteriophenyldiazomethane (21a):** IR (Ar, 15 K) 3208 w, 3115 w, 3085 w, 3040 w, 2062 s, 1601 s, 1499 s, 1488 w, 1430 w, 1383 s, 1208 w, 1387 m, 841 m, 812 w, 747 w, 721 w, 690 w, 641 m, 600 m, 527 w, 432 m cm^{-1}. The deep-red diazo compound was sublimed at −41 °C (10^{-6} torr) and codeposited with argon to form a matrix.

***o*-Fluorobenzaldehyde Tosylhydrazone.** Prepared from *o*-fluorobenzaldehyde (Aldrich) in 76% yield: mp 131–133 °C dec; ^1H NMR (Me_2SO-d_6) δ 2.4 (s, 3 H), 7.0–8.0 (m, 8 H), 8.2 (s, 1 H), 11.7 (s, 1 H); mass spectrum (16 eV), *m/z* (relative intensity) 292 (M^+, 13.2), 156 (13.7), 137 (17.0), 136 (36.9), 108 (100.0), 107 (23.5), 92 (25.1), 91 (21.8). Anal. ($C_{14}H_{13}FN_2O_2S$): C, H, F, N, S.

***o*-Fluorophenyldiazomethane (19b):** IR (Ar, 15 K) 3218 w, 3140 w, 2070 s, 1619 m, 1590 m, 1528 m, 1506 s, 1462 s, 1407 m, 1387 s, 1242 s, 1189 m, 1091 m, 1038 w, 928 w, 849 w, 832 w, 802 m, 747 s, 716 w, 645 w, 628 m, 558 w, 542 w, 488 m, 432 m cm^{-1}; UV (Ar, 15 K) λ_{max} 308, 300, 295, 289, 274, 268, 221, 216 nm. The orange diazo compound was sublimed at −41 °C (10^{-6} torr) and codeposited with argon to form a matrix.

α-Deuterio-*o*-fluorobenzaldehyde Tosylhydrazone. Prepared from α-deuterio-*o*-fluorobenzaldehyde in 50% yield: mp 130–133 °C; ^1H NMR ($CDCl_3/Me_2SO$-d_6) δ 2.4 (s, 3 H), 6.8–8.0 (m, 8 H), 11.2 (s, 1 H); mass spectrum (16 eV), *m/z* (relative intensity) 293 (M^+, 29.7), 138 (26.1), 137 (100.0), 109 (99.2), 92 (23.9), 292 not detected.

α-Deuterio-*o*-fluorophenyldiazomethane (29): IR (Ar, 15 K), 3080 w br, 3040 w, 2281 w, 2070 s, 1622 m, 1581 w, 1515 m, 1499 s, 1458 m, 1361 w, 1346 s, 1223 s, 1089 m, 1036 w, 927 w, 829 m, 819 m, 748 s, 619 m, 551 w, 540 w, 506 vw, 498 vw, 379 w cm^{-1}. The orange diazo compound was sublimed at −41 °C (10^{-6} torr) and codeposited with argon to form matrix.

***o*-Chlorobenzaldehyde Tosylhydrazone.** Prepared from *o*-chlorobenzaldehyde (Aldrich) in 75% yield: mp 142–144 °C; ^1H NMR ($CDCl_3/Me_2SO$-d_6) δ 2.4 (s, 3 H), 7.2–7.9 (m, 8 H), 8.3 (s, 1 H), 11.5 (s, 1 H); mass spectrum (16 eV), *m/z* (relative intensity) 310 (M^+, 2.4), 308 (M^+, 7.1), 156 (26.8), 154 (17.5), 152 (56.0), 126 (31.4), 124 (100.0), 92 (48.8), 91 (25.0), 89 (74.7); Anal. ($C_{14}H_{13}ClN_2O_2S$): C, H, N.

***o*-Chlorophenyldiazomethane (19a):** IR (Ar, 15 K) 3120 w, 2065 s, 1590 m, 1488 s, 1442 m, 1372 s, 1281 m, 1203 w, 1164 w, 1121 m, 1050 m, 1039 s, 745 s, 713 m, 628 m, 547 w, 470 m, 428 m cm^{-1}; UV (Ar, 15 K) λ_{max} 312, 302, 299, 282, 278, 228, 223, 217 nm. The orange diazo compound was sublimed at −19 °C (10^{-6} torr) and codeposited with argon to form a matrix.

2,4,6-Triphenyl-1,3,5-triazabicyclo[3.1.0]hexane.[59] Methanol (300 mL) was cooled to 0 °C and saturated with ammonia for 1 h. The solution was cooled to −10 °C, saturated with ammonia for an additional 15 min, and then cooled to −40 °C. A solution of *tert*-butyl alcohol (17.5 mL) and *tert*-butyl hypochlorite (17.5 mL, 0.145 mol)[60] was added dropwise to the methanolic ammonia solution over a 30-min period. The resulting chloramine solution was warmed to −10 °C and treated dropwise with 25 mL (0.246 mol) of benzaldehyde. After 1.5 h, the cooling bath was removed and the yellow solution allowed to stand at room temperature overnight. The precipitate that formed was collected and recrystallized from 95% ethanol, affording 3.2 g (10 mmol, 12%) of fine white needles: mp 157–159 °C [lit. mp 160–162 °C]; ^1H NMR ($CDCl_3$) δ 2.64 (br s, 1 H), 3.24 (s, 1 H), 5.28–5.67 (m, 2 H), 7.23–7.67 (m, 15 H).

Phenyldiazirine (1).[61] 2,4,6-Triphenyl-1,3,5-triazabicyclo[3.1.0]-hexane (3.2 g, 10 mmol) suspended in methanol (20 mL) at 0 °C was treated with a solution of 1 mL of *tert*-butyl hypochlorite in 3 mL of *tert*-butyl alcohol over a period of 15 min. After stirring at 0 °C for 1 h, the resulting clear solution was stirred at room temperature for 20 min and then poured into 250 mL of 0.05 M aqueous sodium metabisulfite. The solution was extracted with 10-mL portions of petroleum ether, and the combined extracts were dried, filtered, and evaporated. The residue was purified by preparative thin-layer chromatography. The top band eluting with petroleum ether (bp 35–60 °C) afforded 0.94 g (8 mmol, 80%) of diazirine **1** as a pale-yellow oil: IR (Ar, 15 K) 3099 w, 3077 m, 3036 m, 3018 w, 1627 s, 1616 m, 1610 s, 1594 m, 1583 s, 1550 w, 1500 s, 1456 s, 1355 w, 1331 w, 1290 w, 1228 w, 1182 w, 1105 w, 1082 m, 1035 m, 997 m, 989 m, 978 m, 909 w, 815 m, 802 w, 753 s, 695 s, 599 s, 543 m cm^{-1}; UV (Ar, 15 K) λ_{max} 381, 378, 375, 373, 369, 360, 353, 350, 342, 228 sh, 215 nm; ^1H NMR (CCl_4) δ 1.92 (s, 1 H),

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6.72–6.97 (m, 2 H), 7.10–7.30 (m, 3 H). The sample was pulse deposited as a gaseous mixture in argon.

3-Chloro-3-phenyldiazirine (17c).[62] A mixture of sodium chloride (14 g) in 5.25% sodium hypochlorite solution (700 mL) in a pressure equalizing addition funnel was added over 15 min to a mechanically stirred solution of benzamidine hydrochloride (12.4 g, Aldrich) and sodium chloride (20 g) in hexanes (150 mL) and dimethyl sulfoxide (200 mL) in a 3-L, round-bottom, three-neck flask at 0 °C. After stirring an additional 30 min, the crude reaction mixture was extracted with ether (3 × 75 mL); the combined organic layers were washed with water (3 × 50 mL) and saturated aqueous sodium chloride (1 × 50 mL). Stirring the organic phase with saturated aqueous sodium bisulfite solution (40 mL) for 45 min removed benzaldehyde. The aqueous and organic layers were separated, and the aqueous layer was extracted with pentane (3 × 20 mL); the combined organic layers were dried over Na_2SO_4 and filtered, and the solvent was removed in vacuo to give a pale-yellow, sweet-smelling liquid. Distillation (30–35 °C, 0.1 torr) gave the pure diazirine (6.2 g, 51%). CAUTION, the distillation temperature must not exceed 35 °C, as the diazirine decomposes explosively: IR (Ar, 15 K) 3075 w, 1602 m, 1571 s, 1497 m, 1448 m, 1260 m, 1109 w, 1084 w, 1039 m, 1013 s, 910 s, 758 s, 690 s, 664 m, 543 m cm^{-1}; UV (Ar, 12 K) λ_{max} 389, 383, 380, 377, 368, 363, 360, 358, 245 sh, 230 sh, 224 sh, 219 nm; ^1H NMR ($CDCl_3$) δ 7.0–7.1 (m, 2 H), 7.3–7.4 (m, 3 H); ^{13}C NMR (Me_2SO-d_6/$CDCl_3$) δ 47 (diazirine carbon). The sample was sublimed at −47 °C (10^{-6} torr) and codeposited with argon to form a matrix.

Tetra-*n*-butylammonium Fluoride (Dry).[63] Heating a three-neck, 500-mL round-bottom flask containing TBAF·$3H_2O$ (30.7 g, Aldrich) to 45 °C at 3×10^{-4} torr for 48 h removed TBAF's water of hydration. The resultant orange salt, which is molten at 25 °C, must be used immediately.

3-Fluoro-3-phenyldiazirine (17b).[64] Stirring 3-chloro-3-phenyldiazirine[62] (15 mmol) and freshly prepared dry tetra-*n*-butylammonium fluoride[63] (60 mmol) with a mechanical stirrer at room temperature under nitrogen for 20 h produced a pale-orange crystalline mass. The solution was quenched with water at 0 °C, extracted with pentane (3 × 50 mL), and dried over Na_2SO_4. Removal of the pentane in vacuo left a pale-yellow, sweet-smelling oil. Distillation (30 °C, 0.1 torr) gave the pure diazirine (0.6 g, 29%). CAUTION, the distillation temperature must not exceed 35 °C, as the diazirine decomposes explosively: IR (Ar, 15 K) 3080 w, 1595 m, 1568 m, 1558 w, 1499 m, 1449 w, 1302 s, 1189 w, 1170 m, 1167 s, 1160 m, 1101 w, 1075 m, 1038 w, 1008 m, 906 w, 753 s, 713 w, 689 s, 659 w, 555 m, 548 m cm^{-1}; UV (Ar, 15 K) λ_{max} 386, 380, 376, 373, 370 sh, 368 sh, 366, 360, 243 sh, 228 sh, 221, 215, 211 sh nm; ^1H NMR ($CDCl_3$) δ 7.1–7.2 (m, 2 H), 7.3–7.5 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 71 (diazirine carbon). The sample was sublimed at −57 °C (10^{-6} torr) and codeposited with argon to form a matrix.

Diazoacetophenone (14).[65] An ethereal solution of approximately 1.5 g (36 mmol) of diazomethane was treated with 5 mL of triethylamine followed by 4.2 mL (5.1 g, 36 mmol) of benzoyl chloride and stirred at 0 °C for 1 h. The suspension was then stirred at room temperature overnight, filtered, and evaporated. The residue was recrystallized from a mixture of 20 mL of pentane and 20 mL of ether, affording 3.04 g (21 mmol, 58%) of light-yellow plates, mp 45–46.5 °C. A sample was recrystallized from pentane prior to deposition: mp 46–47 °C [lit. mp 47.5–48.5 °C]; IR (Ar, 15 K) 2110 s, 1645 m, 1454 m, 1376 s, 1369 s, 1333 w, 1316 w, 1227 m, 1190 w, 1011 m, 695 m, 678 w cm^{-1}; ^1H NMR (CCl_4) δ 5.90 (s, 1 H), 7.32–7.53 (m, 3 H), 7.60–7.83 (m, 2 H). The sample was sublimed at 5 °C (10^{-6} torr) and codeposited with argon to form a matrix.

7-Acetoxynorbornadiene (9). 7-Acetoxynorbornadiene (Frinton Labs) was purified by vacuum distillation (bp 50–55 °C, 20 torr) and then column chromatography (SiO_2, Et_2O) prior to use: ^1H NMR ($CDCl_3$) δ 1.95 (s, 3 H), 3.63 (m, 2 H), 4.60 (br s, 1 H), 6.5–6.9 (m, 4 H). The strawberry-smelling liquid was sublimed at −29 °C (10^{-6} torr) and codeposited with argon to form a matrix.

2-Diazobicyclo[3.2.0]hepta-3,6-diene (31). The synthesis of this compound has been reported previously.[38]

Dichlorovinylene Carbonate.[66] Ethylene carbonate (186 g, 2.1 mol, Aldrich) was slurried with 400 mL of carbon tetrachloride in a quartz vessel. The mixture was irradiated with a G.E. 275-W sun lamp while chlorine was introduced through a gas dispersion tube at such a rate so as to maintain a moderate reflux. The photolysis was continued until the ethylene carbonate had been exhaustively chlorinated (approximately 2 days), as determined by ^1H NMR. Distillation afforded 384 g (1.7 mol, 81%) of tetrachloroethylene carbonate, bp 150–166 °C.

A zinc–copper couple was prepared by adding 85 g of zinc powder to a solution of 5 g of cupric acetate in 150 mL of glacial acetic acid at 55 °C.[67] After 1 min of vigorous stirring, the reaction mixture was rapidly cooled, and the solvent was aspirated with a glass-fritted tube. The solid residue was washed with anhydrous ether (4 × 100 mL) and dried under a stream of nitrogen.

A vigorously stirred solution of 95 g (0.42 mol) of tetrachloroethylene carbonate in 200 mL of anhydrous ether was treated with 70 g of the zinc–copper couple. After stirring and refluxing overnight, the reaction mixture was filtered through Celite, washed with brine, dried over $MgSO_4$, and distilled, affording 48 g (0.31 mol, 75%) of dichlorovinylene carbonate: bp 40–47 °C/10 torr [lit.[66] bp 40 °C/10 torr].

3a,7a-Dichloro-3a,4,7,7a-tetrahydro-4,7-etheno-1,3-benzodioxol-2-one.[68] A solution of dichlorovinylene carbonate (5 mL) and acetophenone (3 g) in benzene (330 mL) was degassed and photolyzed under argon with stirring for 48 h with a 450-W high-pressure Hanovia mercury-arc lamp in a Pyrex immersion well. The solvent was then removed under reduced pressure and the residue extracted with 140 mL of boiling methylcyclohexane. After standing overnight, the methylcyclohexane solution was decanted from the precipitated material and distilled at reduced pressure. The distillation was continued until most of the acetophenone had been removed, and the residue was then transferred to a sublimation apparatus. Sublimation at 80 °C/20 torr followed by recrystallization from hexane afforded 1.3 g of the dichloroethenobenzodioxolone: mp 190–191 °C [lit.[68] mp 194 °C]; ^1H NMR (CCl_4) δ 4.22–4.52 (m, 2 H), 6.33–6.62 (m, 4 H); IR (KBr) 3075 w, 1840 s, 1805 m, 1268 m, 1213 s, 1070 s, 998 m, 960 m, 902 s, 760 m, 745 m, 692 m cm^{-1}; mass spectrum (16 eV), *m/z* (relative intensity) 156 (5.9), 154 (10.3), 78 (100), no parent ion detected.

Bicyclo[2.2.2]octa-2,5-diene-7,8-dione.[68] Dichloroethenobenzodioxolone (1.3 g, 5.6 mmol) in 25 mL of dioxane and 35 mL of water was warmed to 80 °C for 30 min. The reaction mixture was then cooled and the solvent removed in vacuo. Sublimation of the residue (75 °C/25 torr) and recrystallization from carbon tetrachloride afforded 0.59 g (4.4 mmol, 79%) of the dienedione: mp 100–102 °C [lit.[68] mp 107–108 °C]; ^1H NMR (CCl_4) δ 4.10–4.43 (m, 2 H), 6.52–6.82 (m, 4 H); IR (KBr) 3065 w, 1745 s, 1340 m, 1230 m, 1168 m, 1073 m, 873 m, 758 s, 710 m, 435 m cm^{-1}; mass spectrum (16 eV), *m/z* (relative intensity) 134 (M^+, 2.2), 106 (2.4), 89 (5.4), 78 (100).

Bicyclo[2.2.2]octa-2,5-diene-7,8-dione Monotosylhydrazone. A solution of the bicyclooctadienedione (0.35 g, 2.6 mmol) in 6 mL of methanol was treated with 0.48 g (2.6 mmol) of *p*-toluenesulfonhydrazide (Aldrich; recrystallized from water). After the mixture stirred at room temperature for 2 h, the solvent was removed at reduced pressure and the residue triturated with carbon tetrachloride. Rapid recrystallization from ethanol/toluene afforded 0.52 g (1.7 mmol, 67%) of the monotosylhydrazone, mp 173–178 °C. An analytical sample was further recrystallized from toluene: mp 180–181 °C dec; ^1H NMR (acetone-d_6/$CDCl_3$) δ 2.40 (s, 3 H), 4.07–4.37 (m, 1 H), 4.80–5.10 (m, 1 H), 6.42–6.63 (m, 4 H), 7.28 (AB, 2 H, J = 8 Hz), 7.80 (AB, 2 H, J = 8 Hz), N–H not observed; IR (KBr) 3480 m, 1728 s, 1622 w, 1332 s, 1165 s, 1072 m, 1040 s, 940 m, 872 m, 718 s, 572 m, 548 m cm^{-1}; mass spectrum (70 eV), *m/z* (relative intensity) 274 (0.3), 156 (5), 155 (9), 147 (27), 139 (10), 132 (35), 119 (9), 92 (26), 91 (76), 90 (22), 79 (11), 78 (100), 77 (15), no parent ion detected. Anal. ($C_{15}H_{14}N_2O_3S$): C, H, N.

8-Diazobicyclo[2.2.2]octa-2,5-dien-7-one (33). A solution of 0.10 g (0.33 mmol) of the monotosylhydrazone in 10 mL of dichloromethane was treated with 3.3 mL (0.33 mmol) of 1 N aqueous sodium hydroxide. After the mixture stirred vigorously overnight, the dichloromethane layer was separated and dried over Na_2SO_4. The solvent was removed in vacuo to afford 0.018 g (0.12 mmol, 37%) of the crude diazoketone as a bright-yellow oil. The diazoketone was used without further purification: IR (Ar, 15 K) 3092 w, 3078 w, 3033 w, 2080 s, 1700 s, 1680 m, 1390 s, 1380 s, 1339 m, 1237 w, 1231 w, 1218 w, 1168 w, 1158 w, 1106 m, 1031 s, 950 w, 905 w, 877 m, 762 s, 650 m, 602 w cm^{-1}; ^1H NMR (CCl_4) δ 4.13–4.68 (m, 2 H), 6.67–6.97 (m, 4 H). The sample was sublimed at 25 °C (10^{-6} torr) and codeposited with argon to form a matrix.

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Trimethylsilyl Accelerated Retro-Diels–Alder Reaction: A Quantitative Measure of the β-Effect

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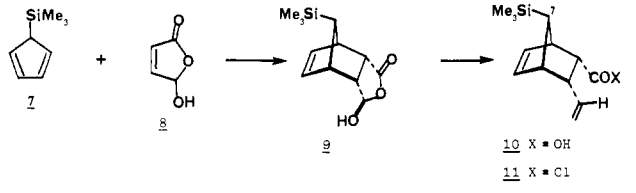
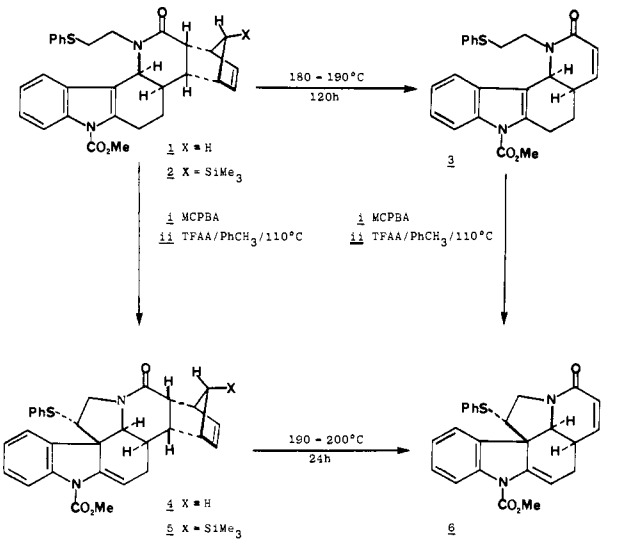
Abstract: The retro-Diels–Alder reaction of **2** proceeds under substantially milder conditions in comparison to its congener, which lacks the trimethylsilyl substituent. When the substrate **14** was used, it was found that the trimethylsilyl group accelerates the retro-Diels–Alder reaction by a factor of approximately 95, relative to the reference **13**. An Arrhenius plot gave E_a, $\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta G^{\ddagger}$.

The retro-Diels–Alder extrusion of cyclopentadiene, as depicted in Scheme I, is part of the strategy we have developed for the synthesis of *aspidosperma*-type indole alkaloids.[1] Heating **1** at 180–190 °C for 120 h (in a sealed tube) resulted in retro-Diels–Alder cyclopentadiene extrusion to give **3** (67%); similarly, heating **4** at 190–200 °C for 24 h gave **6** (>95%). While these extrusions proceed under relatively mild conditions, the reaction times are lengthy. We anticipated that for more highly functionalized sensitive substrates, mild and rapid extrusion conditions would be beneficial. Furan and fulvene Diels–Alder adducts are obvious candidates, except that they are probably too delicate to survive the various electrophilic conditions used in this chemistry and offer other sites of unwanted reactivity. An intriguing solution to this problem, and one of general interest, is to test the following hypothesis, that a trimethylsilyl group trans-coplanar to the C–C bonds which are being broken in the retro-Diels–Alder reaction would lower the activation energy of the extrusion process by virtue of charge stabilization β to the $SiMe_3$ group (Scheme II).[2] The following experiments were conducted to test this idea.

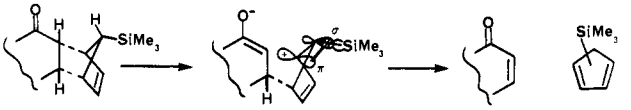
5-(Trimethylsilyl)cyclopentadiene (**7**)[3] reacted with 5-hydroxybutenolide (**8**) at 20 °C to give an 8:1 mixture of Diels–Alder adducts ($SiMe_3$ regioisomers), which on recrystallization gave the pure lactol **9** (78%). Exposure of **9** to $CH_3P^+Ph_3I^-/NaH/Me_2SO$ resulted in the crystalline acid **10** (94%), which was converted into the corresponding acid chloride **11**, using $SOCl_2/Et_2O/DMF$ (catalyst).



Scheme I



Scheme II



The imine **12** was treated with the acid chloride **11** in toluene/*i*-Pr_2NEt/110 °C (identical conditions to those used to give **1**, in the 7-H series) to give **2** (71%) and the α,β-unsaturated lactam **3** (3%). Even under these milder conditions (cf. 180–190 °C for **1** into **3**) a small but readily detectable amount of retro-Diels–Alder reaction has taken place. Heating **2** in toluene/180–190 °C/7 h (sealed tube) gave **3** (ca. 100%). The contrast with the 7-H series, 180–190 °C for 120 h, is dramatic.

Conversion of **2** into **5** with the usual Pummerer conditions ($MCPBA/CH_2Cl_2$ oxidation to the derived sulfoxide, TFAA/110 °C/1.5 h) gave **5** (15%) and the retro-Diels–Alder product **6** (67%). Even conducting the Pummerer reaction at 70 °C gave **6** as the major product. Clearly, the 7-trimethylsilyl group has a substantial accelerating effect. To put this electronic effect on a more quantitative footing, we attempted to study the kinetics of the extrusion process. The *aspidosperma*-type indole alkaloids depicted in Scheme I did not prove to be amenable to first-order

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