work which indicated that **2** is about 1 kcal/mol more stable than *tert*-butyl and **3** is of approximately the same stability as *tert*-butyl.[11,12] The present results indicate that **2**, **3**, and **4** are less stable than *tert*-butyl by *ca.* 1.2, 2.2, and 8.4 kcal/mol, respectively.

A similar correlation between log $(k_{I}/k_{Br})_{cor}$ and $D(R-I)$ is shown in Figure 3 which allows an estimation of the heretofore unreported C–I bond dissociation energies for the bridgehead iodides (Table II). The line is fit best by eq 5 but since there are fewer dependable $D(R-I)$ values for model compounds in the literature the corresponding extrapolated values for the bridgehead iodides are less reliable.[18] The same trends are, however, apparent with 1-iodoadamantane having a slightly larger bond dissociation than *tert*-butyl iodide while 1-iodobicyclo[2.2.1]heptane more closely resembles a primary iodide.

$$D(R-I) = -5.893 \log (k_{I}/k_{Br})_{cor} + 49.82 \qquad (5)$$

Experimental Section

Except for the bridgehead iodides all of the chemicals employed in this study were purchased from commercial sources and purified by either distillation or recrystallization until greater than 99% pure as determined by gas–liquid phase chromatography (glpc). 1-Iodoadamantane was synthesized by the procedure of Schleyer and Nicholas,[19] mp 76.4–77.1 (lit.[19] 75.3–76.4). The starting 1-bromoadamantane was purchased from Aldrich Chemical Co. 1-Iodobicyclo[2.2.2]octane was prepared by the method of Suzuki and Morita,[20] bp 58–60° (0.4 mm) (lit.[20] mp 27.5–28.5°); the compound crystallized when placed in an ice bath but remelted upon standing at room temperature. Glpc analysis showed the presence of 1.53% by weight of 1-chlorobicyclo[2.2.2]octane; allowance for this unreactive contaminant was made in the calculation of the relative rate. 1-Iodobicyclo[2.2.1]heptane was formed by treating the 1-chloro compound[21] with lithium and treating the 1-norbonyllithium thus formed with iodine in ether at 0° according to the method of Lansbury, *et al.*,[22] bp 63–65° (7 mm) (lit.[22] bp 75° (10 mm)). The analytical procedure for determining the relative rates reported in Table I has been described in a previous paper.[1]

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(18) The $D(R-I)$ value for isopropyl iodide was not considered in drawing the line in Figure 3. The authors feel that the reported value of 53 kcal/mol is too large and that a more realistic value would place the $D(R-I)$ of this secondary iodo compound somewhere between those reported for ethyl and *tert*-butyl iodide rather than at the value of ethyl iodide.

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(20) Z. Suzuki and K. Morita, *J. Org. Chem.*, **32**, 31 (1967), and previous papers.

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Photolysis of Matrix Isolated 1,3-Cyclohexadiene, *cis*-1,3,5-Hexatriene, and *trans*-1,3,5-Hexatriene[1]

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Abstract: Ultraviolet and infrared spectroscopy have been used to study the photochemistry of 1,3-cyclohexadiene (I), *cis*-1,3,5-hexatriene (II), and *trans*-1,3,5-hexatriene (III) suspended in argon matrices at 20°K. It was found that I photolyzed rapidly and irreversibly to II, which photolyzed slowly and irreversibly to III and several thermally unstable photoproducts. Various possibilities are considered for the latter and 1,2,4-hexatriene (IV) and *exo*-2-vinylbicyclo[1.1.0]butane (XI) are suggested as likely candidates. Surprisingly, III was found to be photostable under these conditions.

The photochemistry of 1,3-cyclohexadiene (I) and the valency isomeric *cis*-1,3,5-hexatriene (II) and *trans*-1,3,5-hexatriene (III) has been the subject of considerable interest.[3] Vapor-phase photolysis of I or mixtures of II and III were reported to yield hydrogen, a mixture of C_2 hydrocarbons, 1,2,4-hexatriene (IV), benzene, and polymer.[4] In addition I, II, and III were found to be photochemically interconvertible. It was suggested[4c,d] that the formation of IV and the conversion of I to II and III occur through electronically excited states, while all other photolysis products arise from vibrationally excited ground states. Although only small amounts of I were observed from photolysis of II or III in the vapor phase, it was presumed to be the intermediate in their conversion to benzene. This overall reaction was quenched by pressure indicating the intermediacy of a vibrationally excited S_0 state, but the question of whether the initial cyclization to I occurred through an electronically excited state could not be answered unambiguously. Unfortunately in these studies, the different roles of II and III could not be discerned with certainty since mixtures of the two were employed. In solution brief irradiation of I was reported[5] to yield

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(3) (a) R. Srinivasan, *Advan. Photochem.*, **4**, 113 (1966); (b) W. G. Dauben, *Pure Appl. Chem.*, **9**, 539 (1964); (c) M. Mousseron, *Advan. Photochem.*, **4**, 195 (1966); (d) L. F. Fieser and M. Fieser, "Steroids," Reinhold, New York, N. Y., 1959, p 90; (e) G. J. Fonken in "Organic Photochemistry," O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1967, p 197.

(4) (a) R. Srinivasan, *J. Amer. Chem. Soc.*, **82**, 5063 (1960); (b) R. Srinivasan, *ibid.*, **83**, 2806 (1961); (c) R. Srinivasan, *ibid.*, **84**, 3982 (1962); (d) R. Srinivasan, *J. Chem. Phys.*, **38**, 1039 (1963).

(5) R. J. De Kock, N. G. Minnaard, and E. Havinga, *Recl. Trav. Chim. Pays-Bas*, **79**, 922 (1960).

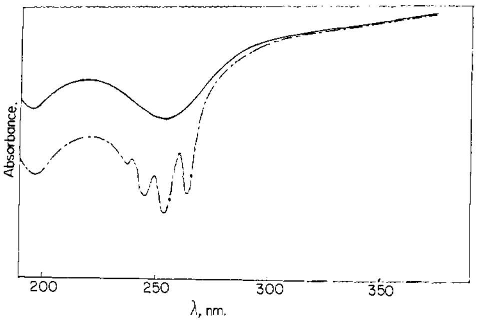
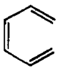
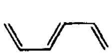


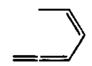
Figure 1. Ultraviolet spectra of matrix isolated 1,3-cyclohexadiene (I) before (———) and after (— — — -) 4 min of photolysis.

III as the major product, possibly through the intermediacy of II. Irradiation of a mixture of II and III failed[6] to yield I, although problems with polymer formation made identification of small amounts of I difficult. Prolonged irradiation of I in solution led to the formation of bicyclo[3.1.0]hex-2-ene (V) and 3-vinylcyclobutene (VI), which were suggested to form *via* II and III.[7]

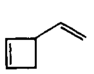

I


II


III


IV


V


VI

The photochemistry of a wide variety of derivatives of I, II, and III has received even more attention.[2] In addition to derivatives of all the photoproducts observed in the parent systems bicyclo[2.2.0]hexanes have also been observed.[2,8] A bicyclo[2.1.1]hexane was also reported,[9] but this was later shown to be in error.[10] The effect of substitutents on the photoproducts from these systems is not well understood nor are many of the mechanistic details of the photochemical processes. As part of our continuing interest[11] in the photochemistry of valency isomeric polyenic systems, we wish to present our results on the photolyses of matrix isolated I, II, and III at 20°K, which furnish information on the primary photochemical processes in these systems.

Results

Photolysis of I at 20°K in an argon matrix with $NiSO_4$ filtered light from a medium-pressure mercury arc was monitored in two ways. Deposition of I in argon (M/R = 1000) yielded a matrix which displayed a broad ultraviolet absorption band with a maximum at 255 nm and end absorption, with a suggestion of a maximum at 195 nm. After 2 min of photolysis the ultraviolet spectrum underwent a drastic change, absorbance increased almost 50% in the range 190–270 nm, and new bands began to appear with maxima at 263, 253, 244, and 237 nm. These changes continued for another 6 min of photolysis until the ultraviolet spectrum was identical with that of II, as shown in Figure 1. Continued irradiation led to a decrease in absorbance in the range 230–270 nm and an increase in the range 230–190 nm, with the eventual appearance of a broad absorption with a maximum around 200 nm. However, even after 70 min of photolysis, the spectrum displayed small maxima at 263, 253, and 244 nm.

In order to build up sufficient concentrations of photoproducts for detection by infrared spectroscopy, deposition of I in an argon matrix (M/R = 100–500) was accomplished in stages with 30-min photolyses between each deposition. After one 30-min photolysis the appearance of new infrared absorption bands was observed and after a total of 2 hr of photolysis a large number of new bands were displayed in the spectrum, as listed in Table I, although a large fraction of I still remained. After the photolysis the cryotip cold window was warmed to room temperature and the matrix allowed to evaporate. The window showed no residual absorption. The sample was pumped through a liquid nitrogen cooled trap, mixed with argon, and redeposited at 20°K.[12] Many of the bands which were in the infrared spectrum of the photolysis product had decreased markedly in relative intensity or even disappeared entirely, as indicated in Table I. New absorption bands appeared which corresponded to bands in the infrared spectrum of III. Every infrared band which did not decrease in relative intensity after warm-up also appears in the infrared spectrum of II. The bands which did change in intensity are all observed in the photolysis products of II, *vide infra*, and are due to species which are presumably formed directly from II,[13] and which are responsible for the increase in ultraviolet absorption in the 230–190-nm range on prolonged photolysis of I.

Table I. Infrared Absorption Bands of 1,3-Cyclohexadiene (I) and of Its Photolysis Products (cm^{-1})[a]

I			Photolysis products		
3071 (msh)	1615 (w)	1060 (w)	3108 (m)	1295* (w)	802* (w)
3060 (vs)	1447 (m)	1020 (w)	2150* (w)	1190 (w)	765* (w)
3020 (w)	1436 (m)	997 (w)	2140* (w)	1142* (w)	715* (w)
	1419 (w)	949 (m)	1825 (m)	1025* (w)	680* (w)
2960 (vs)	1413 (w)	926 (s)	1650* (w)	1015 (m)	603 (s)
2906 (msh)	1381 (m)	850 (w)	1630 (w)	990 (s)	560* (w)
2888 (s)	1335 (w)	746 (s)	1625* (w)	908 (vs)	510* (w)
2840 (s)	1246 (m)	658 (vs)	1490* (w)	845* (w)	390* (w)
2820 (w)	1184 (w)	641 (w)	1459 (s)	840* (w)	350 (w)
1720 (w)	1168 (m)	473 (s)	1365 (w)	820 (m)	
1710 (w)					

[a] An asterisk designates those bands which decreased markedly after warm-up and redeposition (see text).

Photolysis of II was performed and monitored exactly as for I. Changes in the ultraviolet spectrum of II were exactly the same as those outlined after prolonged photolysis of I and are displayed in Figure 2. The residual absorption maxima at 263, 253, and 244 nm are most probably due to the formation of III, whose ultraviolet spectrum displays virtually the same maxima

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(6) G. J. Fonken, *Tetrahedron Lett.*, 549 (1962).

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(9) K. J. Crowley, *ibid.*, **86**, 5692 (1964).

(10) J. Meinwald, A. Ackell, and K. L. Erickson, *ibid.*, **87**, 3532 (1965).

(11) P. Datta, T. D. Goldfarb, and R. S. Boikess, *ibid.*, **91**, 5429 (1969).

(12) During this treatment the sample was at room temperature for several hours.

(13) The possibility that these bands are due to one or more species derived directly from I, which do not absorb in the ultraviolet, seems unlikely, particularly since they also appear directly from II and form more slowly from I than does II.

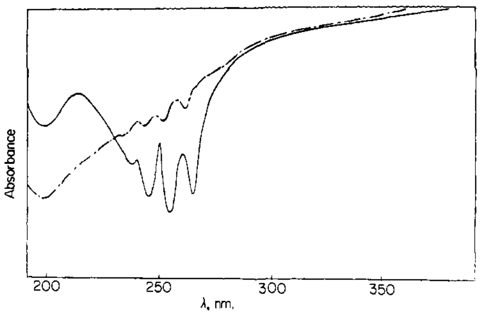


Figure 2. Ultraviolet spectra of matrix isolated *cis*-1,3,5-hexatriene (II) before (———) and after (— — —) 1 hr of photolysis.

as does that of II, although alternatively they may be due to unphotolyzed or regenerated II.

Table II. Infrared Absorption Bands of *cis*-1,3,5-Hexatriene (II) and of Its Photolysis Products (cm^{-1})[a]

II		Photolysis products					
3110 (m)	1365 (w)	3085* (m)	2816* (w)	1295* (w)	765* (m)
3103 (w)	1325 (w)	3056* (m)	2150* (w)	1185* (w)	750* (w)
3060 (m)	1235 (w)	3050 (w)	2145* (w)	1142* (w)	730* (m)
3035 (w)	1190 (w)	3040* (w)	1960* (w)	1050* (w)	718* (m)
3030 (w)	1015 (m)	3027 (w)	1817 (m)	1025* (w)	685 (m)
3010 (w)	990 (s)	3010 (m)	1650* (w)	1015 (s)	675* (w)
1825 (w)	950 (w)	2994* (m)	1640 (m)	975* (w)	660 (w)
1630 (w)	910 (vs)	2990 (w)	1625* (w)	940 (w)	575* (w)
1610 (m)	820 (w)	2970* (w)	1610 (ms)	916* (m)	550 (w)
1605 (sh)	605 (s)	2960* (w)	1490* (w)	900 (s)	515* (w)
1460 (m)	350 (w)	2934* (w)	1450* (w)	870* (w)	485* (w)
		2880* (w)	1440 (w)	845* (m)	385* (w)
		2865* (m)	1410* (w)	840* (m)	
		2860* (m)	1375* (w)	805* (w)	

[a] An asterisk designates those bands which decreased markedly after warm-up and redeposition (see text).

Table III. Infrared Absorption Bands of *trans*-1,3,5-Hexatriene (III)

3110 (m)	1815 (m)	1305 (m)	1015 (vs)	900 (vs)
3050 (m)	1640 (m)	1285 (m)	990 (w)	687 (s)
3025 (m)	1612 (m)	1260 (w)	965 (w)	660 (w)
3010 (w)	1460 (w)	1143 (m)	950 (sh)	600 (w)
2990 (w)	1440 (m)	1135 (sh)	940 (m)	550 (m)

Monitoring the photolysis of II by infrared spectroscopy after irradiation times as long as 8 hr revealed that only a small fraction of II had been transformed. Nevertheless the appearance of a large number of new bands in the infrared spectrum was observed, as summarized in Table II. One group of absorption bands did not decrease appreciably in relative intensity after the same warm-up-redeposition treatment described for I. All these bands also appeared in the infrared spectrum of III, which is summarized in Table III. The other group of bands decreased markedly in relative intensity or disappeared entirely after warm-up and redeposition. The extensive number of such bands and the large differences in the extent of their intensity decreases make it appear that they may be attributed to more than one compound. While it was difficult to ascertain the extent of decrease for weak bands which disappeared after warm-up, it was clear that relatively strong bands at 2155, 916, 840, and 727 cm^{-1} decreased rather more drastically than did others of about the same initial intensity at 1960, 845, 805, 765, 750, and 718 cm^{-1}. This is illustrated in Figure 3 for one region of the spectrum. After redeposition, bands from II had increased more than bands from III and no new bands has appeared. Observation of the growth of the bands during the photolysis failed to reveal any suggestion of formation of any product at the expense of another; only bands of II decreased. Although difficult to ascertain with accuracy, it seemed that no one group of bands appeared noticeably more rapidly than any other. This was not the case in the prolonged photolysis of I, where not nearly as many bands apppeared and none of the ones that did could be assigned to III. This may be due to formation of II from I in a conformation which does not favor conversion to III or some of the other photoproducts and which converts only slowly, because of rotational restrictions by the matrix, to more favorable conformations.

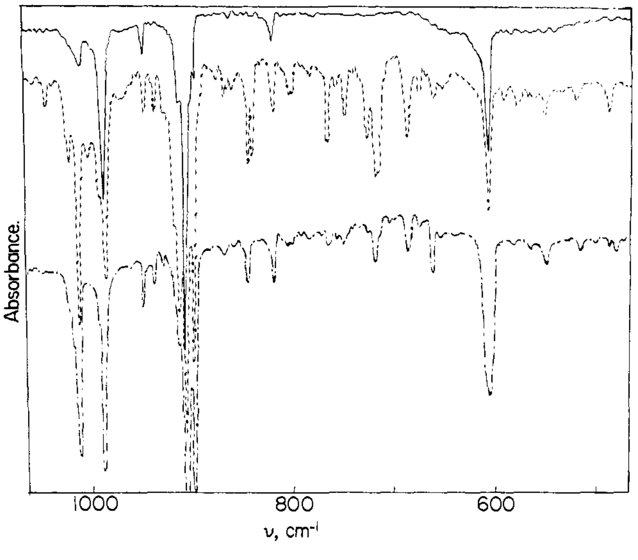


Figure 3. Infrared spectra of matrix isolated II before (———) and after (------) 8 hr of photolysis and after (–·–·–·–) warm-up and redeposition.

Surprisingly, despite the virtual identity of the ultraviolet absorption spectra of II and III, photolyses of argon matrices (M/R = 100–1000) of III for periods as long as 8 hr did not result in any change detectable by ultraviolet or infrared spectroscopy.

Discussion

A picture of the photochemical pathways followed by these systems in the matrix has emerged and is summarized in Scheme I. These results differ in several ways from those of previous workers[3–7] under other conditions. The photochemical interconvertibility reported[4c,d] for I, II, and III in the vapor phase is absent; rather III and probably also the thermally unstable

Scheme I

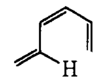
$$\begin{tikzcd}
\mathrm{I} \arrow[r, "h\nu", "\text{fast}"'] & \mathrm{II} \arrow[r, "h\nu", "\text{slow}"'] \arrow[d, "h\nu", "\text{slow}"'] & \mathrm{III} \\
 & \text{thermally unstable species} &
\end{tikzcd}$$

species represent dead ends under our conditions. Presumably at higher temperatures II would be regenerated from at least one of the transients thermally and therefore III would be the main product detected from photolysis of I or II. This has been observed in the solution photolysis of I.[5] The suggestion[4c,d] that formation of I from photolysis of a mixture of II and III in the vapor phase occurs *via* vibrationally excited S_0 states is reinforced by the nonoccurrence of this process under our conditions, where vibrationally excited ground states are rapidly deactivated. An alternative possibility is that rotational restrictions imposed by the matrix prevent II from achieving the necessary cisoid–cisoid conformation for ring closure. This seems less likely since II produced from I should have virtually the correct orientation for recyclization; yet no evidence for this process could be seen.

The failure of III to convert to II under our conditions suggests that this isomerization also occurs by internal conversion to an excited S_0 state, which would be deactivated by the matrix before it could isomerize. Alternatively conformational restrictions imposed by the matrix could again be responsible for the absence of the isomerization. This seems less likely since the reverse isomerization, cis to trans, is observed.

The absence of absorption bands due to benzene, ethylene, or acetylene is consistent with the suggestion[4] that these products arise *via* internal conversion to vibrationally excited ground states. The absence of bands which could be attributed to V or VI, both of which are thermally stable[6] and should survive the warm-up, suggests that the efficiency of processes leading to their formation is an order of magnitude lower than the efficiency of the processes we are observing. V and VI most probably arise from electronic excited states of II rather than of I since II is formed so rapidly from I, but evidently other pathways accessible to the excited state of II are much more favorable and will predominate during relatively short photolysis times.

The nature of the thermally unstable photoproducts has not been rigorously established but several candidates suggest themselves. It has been reported[4b] that 1,2,4-hexatriene (IV) arises directly from an electronic excited state of II. IV was found to be quite reactive, yielding polymeric material on standing at room temperature. Its infrared spectrum in CCl_4 solution was reported to display bands consistent with the structure at 5.18 (allene), 7.24 (C-methyl), and 11.82 μ (allene) as well as bands due to olefinic C–C and C–H vibrations in the usual regions. Its ultraviolet spectrum displayed a broad intense absorption with a maximum close to 220 nm. We find bands in the infrared spectrum of the photoproducts of II, consistent with all those reported for IV, at 1960 (5.10 μ), 1375 (7.27 μ), and 845 cm^{-1} (11.8 μ). Furthermore, ultraviolet absorption in the 220-nm region increased as the photolysis of II proceeded. The formation of IV is most easily visualized to occur by a 1,5-hydrogen shift in the excited state. Such a shift is possible only when the central double bond is cis, thus the absence of this product from III. It appears that only in the cisoid–transoid conformation VII is the shifting hydrogen close to the terminal carbon to which it becomes bonded. This conformational requirement is probably responsible for the relatively slow formation of IV. The decrease in the relative intensity of bands due to IV after warm-up and redeposition would result from losses due to polymerization of this compound while standing at room temperature for several hours.

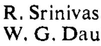


VII

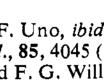
The nature of the other photoproduct or products is an intriguing question which we cannot as yet answer with certainty. Consideration first of possible hydrogen migrations which can occur in the excited state of II but not of III leads us to only one other reasonable possibility: a homodienyl 1,5-hydrogen shift in the cisoid–cisoid conformation yielding 3-(1-propenyl)cyclopropene (VIII). Homodienyl 1,5-hydrogen shifts are known[14] thermal processes, but no example of the type suggested here has been observed and we considered it to be a rather unlikely rearrangement. If it was formed, VIII would be expected to polymerize readily at room temperature[15] and to have infrared absorption bands associated with cyclopropenyl C–H stretches near 3100 cm^{-1}, and double bond stretch around 1640 cm^{-1} as well as bands characteristic of a *cis*-olefin at 1662–1631, 1429–1397, and 730–650 cm^{-1}.[16] Bands in all these regions are observed in the infrared spectrum of the photoproducts of II and diminish or disappear after warm-up.

VIII

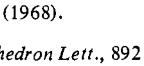
A variety of cyclization pathways might be followed by the excited state of II but not III. For instance, closure to bicyclo[2.2.0]hexane (IX), which is observed[8] in substituted hexatrienes, or to bicyclo[2.1.1]hexene (X), which was incorrectly reported,[9,10] could be envisaged. However, since both IX[17] and X[18] have been prepared and found to be quite stable thermally, these possibilities are ruled out. Bicyclo[1.1.0]butanes have been formed as a minor product in the photolysis of 1,3-butadiene[19] and as the major product in the photolysis of some alicyclic dienes[3b,20] locked in a transoid conformation. This kind of cyclization, which must occur in an electronically excited state, from a transoid conformation of II or III would form a 2-vinylbicyclo[1.1.0]butane (XI). Orbital symmetry considerations[21] suggest that this products arises from a ${}_{\pi}2_a + {}_{\pi}2_a$ cyclization of



IX



X



XI

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the excited state with a disrotatory motion about the developing central bond of the bicyclobutane. This type of closure will place the 2-vinyl group exo when it occurs from II, but endo when it occurs from III. Since considerably more steric interaction is developed when the vinyl group is endo this may serve to rationalize the failure of III to undergo photolysis to this type of product. Many of the bands in the infrared spectrum of the photoproducts, which decrease in intensity after warm-up, are consistent with formation of *exo*-XI. For instance, bands at 3087 and 3056 cm^{-1} are reasonable[22] for cyclopropyl CH_2 stretches in a bicyclobutane, bands between 3000 and 2880 cm^{-1} are reasonable[22] for tertiary C–H stretches in this system and unreasonable[16] for olefinic C–H stretches. Also, bands at 1185, 1142, 975, 840, and 730 cm^{-1} could be assigned[16,18a] to vibrations associated with cyclopropyl rings of a bicyclobutane. A fairly strong band grows in at 916 cm^{-1}, which is in the region usually associated with the CH_2 way of a vinyl group.[16] The ultraviolet spectrum of methyl bicyclobutane-1-carboxylate has been found[23] to have an absorption maximum at 210 nm (ϵ 7000) and the ultraviolet spectra of some vinylcyclopropanes have been found[24] to have maxima around 200 nm. Therefore, it is not unreasonable to expect ultraviolet absorption around 200–210 mμ for *exo*-XI, as is observed in the photolysis products of II.

Thermolysis of alkyl-substituted bicyclobutanes has been found to be a concerted process, in which one ring opens conrotatory and one ring opens disrotatory, thus leading to two products from bicyclobutanes which do not have a C_2 symmetry axis.[25] The activation energy for this kind of process is about 40 kcal/mol and the reaction is rapid at 200°.[26] Introduction of a vinyl group at the 2 position of a bicyclobutane could well lower the activation energy sufficiently to make the thermolysis relatively facile at room temperature, either by conjugation with the transition state in a concerted process or by causing a changeover to a nonconcerted diradical process, which gains from allylic stabilization of the developing radical.[27] In either case, a mixture of II and III would be regenerated.

Thus, although far from rigorously established, it seems that 1,2,4-hexatriene (IV) and *exo*-2-vinylbicyclo[1.1.0]butane (*exo*-XI) are the most likely candidates for the thermally unstable photoproducts of II. Both may be formed only from II; both photoprocesses leading to them have analogies in other systems or under other conditions in the same system; both are compatible with the changes in the infrared and ultraviolet spectra; and both are consistent with the warm-up–redeposition behavior.

Experimental Section

The cryotip refrigerator and all the experimental procedures for performing the photolyses and recording the spectra have already been described.[11]

Samples of 1,3-cyclohexadiene (I) were purified by preparative vapor phase chromatography before use. A mixture of II and III (Chemical Procurement Co.) was purified by the known[28] procedure. Samples purified by preparative vapor phase chromatography were employed.

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Solvolysis of Trans-Fused Bicyclo[6.1.0]nonyl-2 Derivatives[1]

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Abstract: The rates and products of solvolysis of the trans-fused bicyclo[6.1.0]nonyl 2-(3,5-dinitrobenzoates) have been determined. The trans,trans isomer was found to be 1.8×10^4 times as reactive as the trans,cis isomer. This results from the unusual conformation of the latter in which the leaving group lies over the cyclopropane ring. Just as with the corresponding cis-fused derivatives, there is no crossover in products between the two epimers, and the rearrangement products were formed by stereospecific processes. The solvolysis of α-deuterium labeled derivatives also was studied, and only one of the four isomers (cis and trans fused) was found to give deuterium scrambling.

It now seems clear that the solvolysis of cyclopropylcarbinyl derivatives usually leads first to an unrearranged cyclopropylcarbinyl cation.[2] This, in turn, may rearrange to another cyclopropylcarbinyl cation *via* the stereospecific cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement.[3] The conformational effects

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