dropwise, with 7 g (0.013 mol) of propionaldehyde in 25 ml of ether. The mixture was stirred overnight at room temperature and then worked up to give 3.2 g (38%), bp 87–91° (12.5 mm), consisting of a mixture of cis and trans isomers. The trans isomer of 1-(*o*-tolyl)-1-butene was separated by glc on column 1[20] and obtained as a colorless liquid: ir (liq) 1650 (C=C), 1600 (Ar), 1380 (C–CH_3), 964 (*trans*-CH=CH), 744 cm^{-1} (1,2-disubstituted Ar); nmr (CCl_4) δ 1.10 (t, 3, J = 7.1 Hz, CH_3), 2.55 (quintet–doublet of quartets, 2, J = 7.0 Hz, CH_2), 2.28 (s, 3, ArCH_3), 5.75-6.75 (m, 2, =CH), 6.95–7.45 (m, 4, Ar*H*).

Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.69; H, 9.56.

(**c**) *trans*-**1-(*o*-Tolyl)-2-butene (7).** 1-(*o*-Tolyl)-2-butyne was prepared in 58% yield by the action of *o*-tolylmagnesium bromide on 1-bromo-2-butyne and was obtained as a colorless liquid: ir (liq) 1600 (Ar), 1380 (C–CH_3), 743 cm^{-1} (1,2-disubstituted Ar); nmr (CCl_4) δ 1.79 (t, 3, J = 2.5 Hz, ≡C–CH_3), 2.24 (s, 3, ArCH_3), 3.36 (q, 2, J = 2.5 Hz, CH_2), 6.92–7.49 ppm (m, 4, Ar*H*).

Anal. Calcd for $C_{11}H_{12}$: C, 91.61; H, 8.39. Found: C, 91.34; H, 8.24.

A 7.2-g sample of this material was dissolved in 50 ml of ether and added to a solution of 3.55 g of sodium in 150 ml of liquid ammonia. The mixture was stirred for 1.75 hr at the reflux temperature of ammonia, ammonium nitrate was added until the blue color disappeared, and the mixture was worked up to give a middle distillation fraction consisting of 2.9 g of almost pure *trans*-1-(*o*-tolyl)-2-butene (**7**). A pure sample was obtained by glc separation on column 1[20] as a colorless liquid: ir (liq) 1600 (Ar), 1380 (C–CH_3), 968 (*trans*-CH=CH), 745 cm^{-1} (1,2-disubstituted Ar); nmr (CCl_4) δ 1.65 (d, 2, J = 4.6 Hz, =CCH_3), 2.24 (s, 3, ArCH_2), 3.22 (d, 2, J = 4.6 Hz, CH_2), 5.25–5.62 (m, 2, =C*H*), 7.00 ppm (s, 4, Ar*H*).

Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.63; H, 9.46.

(**d**) *cis*-**1-(*o*-Tolyl)-2-butene (8).** Following a literature procedure,[30] a 1.135-g sample of 1-(*o*-tolyl)-2-butyne was dissolved in 25 ml of anhydrous methanol, treated with 0.133 g of 10% palladium on charcoal and 4 drops of quinoline, and hydrogenated at 20 psi. After 7 min the amount of hydrogen corresponding to 1 mol equiv of hydrogen had been absorbed, and the product was worked up to give virtually pure *cis*-1-(*o*-tolyl)-2-butene as a colorless liquid: ir (liq) 1660 (Ar), 1600 (Ar), 744 (1,2-disubstituted Ar), 690 cm^{-1} (*cis*-CH=CH); nmr (CCl_4) δ 1.62–1.80 (m, 3, =CCH_3), 2.23 (s, 3, ArCH_3), 3.20–3.44 (m, 2, CH_2), 5.17–5.83 (m, 2, =C*H*), 7.00 ppm (s, 4, Ar*H*).

Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.42; H, 9.44.

Acknowledgment. This work was supported, in part, by Grant No. GP-4951 from the National Science Foundation and Grant No. 1781-A from the Petroleum Research Fund administered by the American Chemical Society, to whom the authors express their gratitude. They are also indebted to Professor Peter Gaspar for stimulating discussions during the course of this research.

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(30) D. J. Cram and N. L. Allinger, *J. Amer. Chem. Soc.*, **78**, 2518 (1956).

Halogen Abstraction Studies. III. Free-Radical Abstraction of Iodine from Bridgehead Iodides[1,2]

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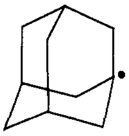
Abstract: The rate of abstraction of iodine from 1-iodoadamantane, 1-iodobicyclo[2.2.2]octane, 1-iodobicyclo[2.2.1]heptane, and *tert*-butyl iodide by the phenyl radical is reported relative to the rate of abstraction of bromine from bromotrichloromethane. All three bridgehead compounds are less reactive than *tert*-butyl iodide. The ease of formation of the adamantyl-1 radical is between that of a typical secondary radical and the *tert*-butyl radical, while the bicyclo[2.2.1]heptyl-1 radical parallels the methyl radical in stability. The intermediate bicyclo[2.2.2]octyl-1 radical resembles the adamantyl species more closely than it does the bicycloheptyl radical. A correction of the relative rates for the slight inductive effect of substituents allows a determination of the bond dissociation energies *D*(R–H) and *D*(R–I) for the bridgehead compounds.

It is well established that the most stable configuration of carbonium ions is a planar, sp^2 hybridized form, while the most favorable geometry of unconjugated carbanions is generally accepted to be a rapidly inverting, pyramidal sp^3 form.[4] The unique position of free radicals, being electronically situated between these two species, has prompted considerable interest in recent years in determining the ease of formation and relative stabilities of the bridgehead free radicals **2**–**4**.[5–12]

$(CH_3)_3C\cdot$

1



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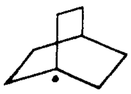

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4

From a study of the rate of bridgehead aldehyde decarbonylation Applequist and Kaplan[11] had con-

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[1] Part II: W. C. Danen and R. L. Winter, *J. Amer. Chem. Soc.*, **93**, 716 (1971).

[2] Acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society (Grant PRF No. 1123-G1) and the Bureau of General Research, Kansas State University, for support of this work.

[3] National Science Foundation Undergraduate Research Participant, summer 1968.

[4] R. C. Fort, Jr., and P. von R. Schleyer, *Advan. Alicycl. Chem.*, **1**, 283 (1966).

[5] A. Oberlinner and C. Ruchardt, *Tetrahedron Lett.*, 4685 (1969).

[6] C. Ruchardt, K. Herwig, and S. Eichler, *ibid.*, 421 (1969).

[7] J. P. Lorand, S. D. Chodroff, and R. W. Wallace, *J. Amer. Chem. Soc.*, **90**, 5266 (1968).

[8] R. C. Fort, Jr., and R. E. Franklin, *ibid.*, **90**, 5267 (1968).

[9] L. B. Humphrey, B. Hodgson, and R. E. Pincock, *Can. J. Chem.*, **46**, 3099 (1968).

[10] I. Tabushi, T. Okada, and R. Oda, *Tetrahedron Lett.*, 1605 (1969).

[11] D. E. Applequist and L. Kaplan, *J. Amer. Chem. Soc.*, **87**, 2194 (1965).

[12] S. F. Nelsen and E. F. Travecedo, *J. Org. Chem.*, **34**, 3651 (1969).

cluded that both **2** and **3** were somewhat more stable than the *tert*-butyl radical **1**. Results from studies of the thermolysis of the bridgehead *tert*-butyl peresters produced the anticipated order of stability **1** > **2** > **3** > **4**, but such perester decomposition studies are complicated by both a large polar effect and the fact that such thermolyses may not occur by a concerted two-bond scission when unstable radicals such as **4** are being formed.[7,8] Recent results on the high-temperature (300°) thermolysis of the bicyclic azo compounds RN═NR indicate a similar ordering but with a surprisingly large difference of 2500 in the relative rate of formation of **1** as compared to **2** while a factor of only 125 differentiates **2** from **4**.[5] *A priori*, the relatively modest amount of strain in the adamantyl-1 as compared to the bicyclo[2.2.1]heptyl-1 radical, a consequence of the fact that free radicals have smaller force constants for out-of-plane bending than do the corresponding carbonium ions,[4,8] would suggest that the adamantyl-1 free radical should resemble a typical planar tertiary species such as **1** more so than nonplanar **4**.

We presently wish to report the rates of abstraction of iodine by the phenyl radical from the corresponding bridgehead iodides relative to the abstraction of bromine from bromotrichloromethane (Table I).[1,13] This method of assessing the relative ease of formation of the radicals **1**–**4** has several advantages, the most significant of which is the assurance that the rates truly reflect the rate of formation of a specific radical site within a molecule even with an unstable species such as **4**. The relative rates can be obtained with a high degree of accuracy not requiring extrapolation, and direct comparison with a variety of other alkyl radicals is possible. Moreover, the influence of polar effects on such iodine abstraction processes has been well defined.[1,13]

Table I. Relative Rates of Abstraction of Iodine from Alkyl Iodides by Phenyl Radical at 60°

Compound	k_I/k_{Br}[a]	$\Sigma\sigma^*$ [b]	$(k_I/k_{Br})_{cor}$[c]
tert-Butyl iodide	1.08[d]	0.00	1.08
1-Iodoadamantane	0.66	−0.31[e]	0.75
1-Iodobicyclo[2.2.2]octane	0.55	−0.27[e]	0.62
1-Iodobicyclo[2.2.1]heptane	0.17	−0.23[e]	0.19
Methyl iodide	0.17	1.47	0.091
Ethyl iodide	0.33	0.98	0.218
Isopropyl iodide	0.58	0.49	0.471
sec-Butyl iodide	0.54	0.39	0.458
Neopentyl iodide	0.24	0.68	0.180

[a] Rate of abstraction of iodine relative to the abstraction of bromine from bromotrichloromethane. [b] Summation of Taft polar substituent constants for the three groups attached to the carbon from which the iodine is abstracted. [c] Relative rate corrected for the influence of inductive effects by application of the Taft relationship with $\rho = +0.184$. [d] Estimated from k_{Br}/k_{Cl} results; see text. [e] Average of several possible values.

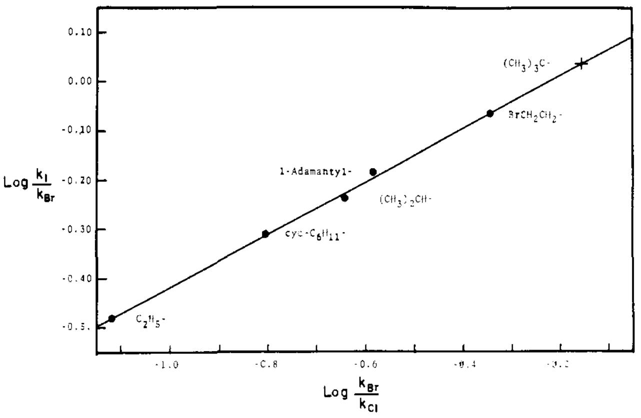

Figure 1. Plot of log k_I/k_{Br} (relative rate of abstraction of iodine from indicated compounds *vs.* bromine from bromotrichloromethane) *vs.* log k_{Br}/k_{Cl} (relative rate of abstraction of bromine from indicated compounds *vs.* chlorine from carbon tetrachloride).

Results

The relative rates listed in Table I were obtained by the competitive technique employed in our earlier studies[1,13] in which the phenyl radical is allowed to react with a large excess of both bromotrichloromethane and iodo compound. The phenyl radicals were

$$\mathrm{RI} + \cdot\mathrm{Ph} \xrightarrow{k_I} \mathrm{R}\cdot + \mathrm{PhI} \qquad (1)$$

$$\mathrm{CBrCl_3} + \cdot\mathrm{Ph} \xrightarrow{k_{Br}} \mathrm{CCl_3}\cdot + \mathrm{PhBr} \qquad (2)$$

generated by decomposition of phenylazotriphenylmethane (PAT) at 60.0 ± 0.10° and the k_I/k_{Br} values calculated from eq 3. The combined yields of iodo-

$$k_I/k_{Br} = \frac{[C_6H_5I][CBrCl_3]}{[C_6H_5Br][RI]} \qquad (3)$$

benzene and bromobenzene were typically 80–90% except in the case of *tert*-butyl iodide in which the reaction solution became deeply colored and the yield of halobenzenes was drastically reduced. Although k_I/k_{Br} for this compound could be estimated at *ca.* 1.0–1.1, it was felt that a more reliable determination of this value was necessary. To this end we determined the rates of abstraction of bromine from a number of alkyl bromides relative to the rate of abstraction of chlorine from carbon tetrachloride. A plot of log k_I/k_{Br} *vs.* log k_{Br}/k_{Cl} for a common series of iodo and bromo compounds produced the linear relationship shown in Figure 1 which, upon extrapolation, yielded a k_I/k_{Br} value of 1.08 for *tert*-butyl iodide. From the slope of *ca.* $^1/_2$ it can be deduced that, not unexpectedly, bromine abstraction by the phenyl radical is about twice as sensitive to structural effects as iodine abstraction.

Discussion

It can be seen from Table I that the relative rate of formation of the various free radicals decreases in the order **1** > **2** > **3** > **4**. However, it would probably be appropriate to correct these values for the inductive effect as compared to **1** in a manner analogous to that attempted in the perester decompositions.[7,8] We have shown in previous work[1] that the relative reactivities of a series of substituted primary iodo compounds can be correlated very well with Taft polar substituent constants. The ρ value of +0.184 obtained for such compounds is much smaller than the −1.6 necessary for the perester series;[8] moreover, the correction to be applied in the present case is in the opposite direction since now an accumulation of electron donating alkyl

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(13) W. C. Danen and D. G. Saunders, *J. Amer. Chem. Soc.*, **91**, 5924 (1969).

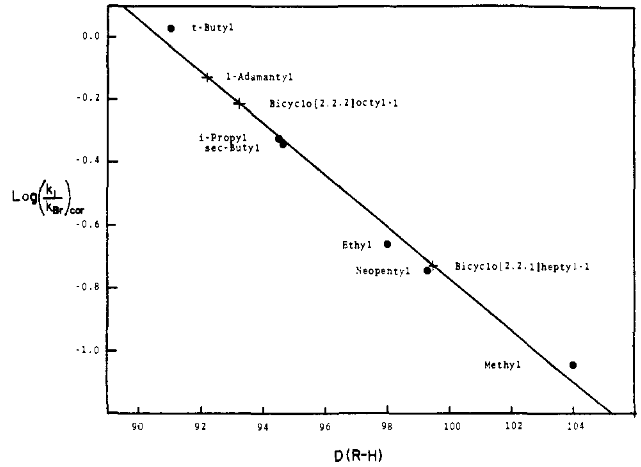


Figure 2. Plot of log corrected relative rate of iodine abstraction *vs.* C–H bond dissociation energies. Values of *D*(R–H) for compounds indicated by dots were obtained from ref 17; values for the bridgehead compounds indicated by crosses are those predicted by extrapolation of the present results.

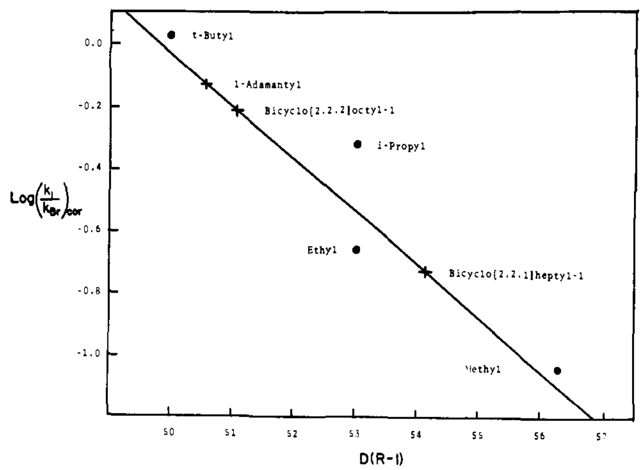


Figure 3. Plot of log corrected relative rate of iodine abstraction *vs.* C–I bond dissociation energies. Values of *D*(R–I) for compounds indicated by dots were obtained from ref 17; values for the bridgehead compounds are those predicted by extrapolation of the present results. The *D*(R–I) value for isopropyl iodide was not considered in constructing the plotted line (*cf.* ref 18).

moieties in the bicyclic systems tends to retard the abstraction of an iodine atom. It is necessary, then, to subtract out the small contribution of the inductive effect from the k_I/k_{Br} values leaving only the effect of the nonplanar geometry to influence the relative rates of formation of **1**–**4**. If one considers the bridgehead iodides as tertiary iodo compounds, $R_1R_2R_3CI$, one can sort out the skeleton of each bridged molecule into simple alkyl groups for which Taft polar substitutent constants σ^* have been assigned.[14] Since this sorting procedure can be accomplished in several different ways for the bicyclic compounds an average $\Sigma\sigma^*$ is listed in Table I and utilized with the $+0.184$ ρ value to produce the corrected relative rates.

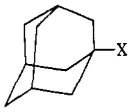
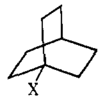
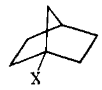
On an absolute basis it is seen from the data in Table I that the adamantyl-1 radical is formed less readily than the *tert*-butyl radical but faster than a typical secondary radical such as isopropyl. On the other extreme, the bicyclo[2.2.1]heptyl-1 radical is formed only with difficulty, the bridgehead compound being as reactive to iodine abstraction on an absolute basis as methyl iodide. Although a fraction of the rate retardation is due to inductive effects the similarity in stabilities between **4** and the methyl radical parallels the results of other studies.[4,15] It can also be seen that 1-iodobicyclo[2.2.2]octane is about as reactive to iodine abstraction as a typical secondary iodide and resembles the adamantyl compound in reactivity much more than it resembles the norbornyl iodide.

A more quantitative comparison of the relative stabilities of **1**–**4** can be made by relating the corrected k_I/k_{Br} values to bond dissociation energies. In a manner analogous to that attempted by Applequist and Kaplan[11] and limited to the same assumptions[16] we have found that a plot of log $(k_I/k_{Br})_{cor}$ for a variety of alkyl iodides *vs.* the best available[17] bond dissociation energies, *D*(R–H), produces a remarkably linear relationship (Figure 2, correlation coefficient = 0.991). Although there are undoubtedly errors of various magnitudes in the literature *D*(R–H) values and in the inherent assumptions, confidence is gained by appreciating that the correlation spans more than an order of magnitude in relative reactivities and $\Sigma\sigma^*$ ranging from $+1.47$ to -0.31. The line in Figure 2 is fit by eq 4 with an average deviation of ±0.5 kcal/mol from which it is possible to obtain the extrapolated

$$D(\text{R–H}) = -12.083 \log (k_I/k_{Br})_{cor} + 90.70 \quad (4)$$

D(R–H) values listed in Table II for the bridgehead positions of the bicyclic compounds. Although no significance can be attached to the final digit in the numbers thus obtained a comparison with the *D*(R–H) values derived by Applequist and Kaplan[11] reveals that the present values are 1.7–2.2 kcal/mol larger in all three cases. The present values are, at least intuitively, more reasonable in that the anticipated order of stability **1** > **2** > **3** > **4** is predicted unlike the earlier

Table II. Extrapolated R–H and R–I Bond Dissociation Energies (kcal/mol), 25°

	D(R–H)	*D*(R–I)
$(CH_3)_3C$—X	(91.0)	(50.0)
	92.2	50.6
	93.2	51.0
	99.4	54.1

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[14] J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, p 222.

[15] F. D. Greene, M. L. Savitz, F. D. Osterholtz, H. H. Lau, W. N. Smith, and P. M. Zanet, *J. Org. Chem.*, **28**, 55 (1963).

[16] *I.e.*, variations in k_I/k_{Br} are due to changes in the activation energy part of k_I, differences in *D*(R–H) are proportional to differences in *D*(R–I), and the Evans–Polani relationship applies. In addition, in this study one must assume the reliability of the procedure for correcting the relative rates for inductive effects.

[17] J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).

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 $(k_\mathrm{I}/k_\mathrm{Br})_\mathrm{cor}$ and $D(\mathrm{R{-}I})$ 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 de-

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

pendable $D(\mathrm{R{-}I})$ 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.

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 $D(\mathrm{R{-}I})$ 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 $D(\mathrm{R{-}I})$ of this secondary iodo compound somewhere between those reported for ethyl and *tert*-butyl iodide rather than at the value of ethyl iodide.

(19) P. von R. Schleyer and R. D. Nicholas, *J. Amer. Chem. Soc.*, **83**, 2700 (1961).

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

(21) R. L. Bixler and C. Niemann, *ibid.*, **23**, 742 (1958).

(22) P. T. Lansbury, V. A. Pattison, J. D. Sidler, and J. B. Bieber, *J. Amer. Chem. Soc.*, **88**, 78 (1966).

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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(2) Address correspondence to this author at the Department of Chemistry, Douglass College, New Brunswick, New Jersey 08903.

(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).