

clohexadecane (7). Using method A the following reagents were combined: 0.82 g (1.0 mmol) of **5**, 30 mL of 1 M $\text{BCl}_3/\text{CH}_2\text{Cl}_2$ solution, and 15 mL of CH_2Cl_2 . Workup gave 0.8 g (~100%) of **7**: ^1H NMR ($\text{Me}_2\text{SO}-d_6\text{-D}_2\text{O}$) showed the complete absence of the $-\text{OCH}_2\text{O}-$ ($\delta \approx 6.0$) moiety. A sample dried at 100°C in vacuo gave the correct elemental analysis for $7 \cdot 2\text{H}_2\text{O}$.

Anal. Calcd for $\text{C}_{40}\text{H}_{44}\text{N}_4\text{O}_{12} \cdot 2\text{H}_2\text{O}$: C, 59.40; H, 5.98; N, 6.93. Found: C, 59.09; H, 5.70; N, 6.82.

Summary

The similar coordination chemistry of Pu(IV) and Fe(III) in vitro and in vivo has led to a biomimetic approach in the synthesis of specific sequestering agents for Pu(IV) and other actinide(IV) ions. The octadentate chelating agents **6** and **7** have been prepared and their coordination properties and biological activity are under investigation. Both **6** and **7** are much less susceptible to hydrolysis than is enterobactin and both **6** and **7** are less sensitive to air oxidation than 2,3-dihydroxybenzoic acid. Qualitative observations have shown that Pu(IV) dissolves in the presence of **6** even at high pH. Since the K_{sp} for $\text{Pu}(\text{OH})_4$ is approximately 10^{-52} ,²⁰ this indicates a formation constant which is greater than 10^{52} for the Pu(IV) complex of deprotonated **6**.

Acknowledgment. This work was supported by the Division of Basic Energy Sciences, U.S. Department of Energy.

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Mechanisms of Photochemical Reactions in Solution. 77. The Effect of Configuration in Some Bicyclic Di- π -methanes with Simple Chromophores

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Abstract: Direct and sensitized irradiations of 5-methylenebicyclo[2.2.1]hept-2-ene and three related di- π -methanes have been conducted. The rearrangement occurring upon direct irradiation of 5-ethylidenebicyclo[2.2.1]hept-2-ene is demonstrated to be nonconcerted. In addition to the expected di- π -methane rearrangement product, 5-(3-methylbut-2-enylidene)bicyclo[2.2.1]hept-2-ene yielded 5-methylene-3-(3-methylbut-2-enylidene)cyclohexene. Of the four compounds investigated, only bicyclo[2.2.1]hept-2-en-5-isopropylimine did not undergo a di- π -methane rearrangement.

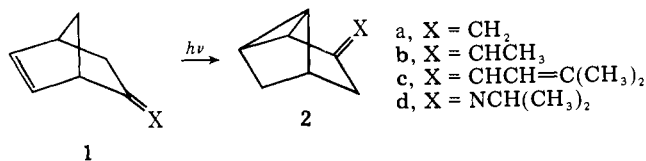
The di- π -methane rearrangement,² exemplified by the reaction in eq 1, has been the subject of continued intensive



investigation both for its own sake and as an example of bichromophoric interaction. In spite of this, relatively few solution-phase examples of di- π -methane rearrangements in which the chromophores are unsubstituted (or alkyl substituted) double bonds have been reported.^{2b} Vapor phase photolyses, many with mercury as sensitizer, have been conducted on several simple di- π -methanes.³ However, experience has shown that vapor- and solution-phase photochemistry of di- π -methanes can be completely different.^{2b,3c,4} Frequently, the participating chromophores of di- π -methanes in solution-phase photolyses are substituted with highly absorbing auxochromes which mask the energetic details of the rearrangement. This and a number of other variables which appear to govern re-

activity (e.g., excited state multiplicity, alternate routes of reaction, and relative orientation of participating chromophores) can be controlled at least partially by judicious design of the reactant molecules.

Herein, we report results from the irradiation of a series of di- π -methanes (**1a-d**) which do not contain extensive auxo-



chromic substituents and in which the relative orientations of the chromophoric groups are rigid and essentially invariant.⁵ The comportment of these compounds is compared to di- π -methanes with similar chromophores of different relative orientations.

Table I. Irradiations of **1** and Their Photoproducts

Run	Concn, M $\times 10^2$	Solvent	Sensitizer (% v/v)	Deoxygenation procedure ^a	Irradiation wavelength, nm	Irradiation time	Conversion, %	Analysis ^b	Monomeric products
1. 1a	11	Cyclohexane		A, 15 min	>220 ^d	27 h	50	E, 65 °C	2a (16%)
2. 1a	2.8	Cyclohexane (19 mL)	Acetophenone (5%)	A, 20 min	305 ^e	36 h	51	E, 65 °C	2a (1.8%)
3. 2a	4.7	Pentane		A, 10 min	>220 ^d	20 h	48	E, 75 °C	1a (5.5%)
4. 1b (16.3/1)	1.45	Cyclohexane (1 mL)		A, 30 min	>220 ^d	32 min	15	G, 65 °C	1b (8.0/1); 2b (0.7% and 2.2%); 3b (1.5%)
5. 1b (2.9/1)	1.45	Cyclohexane (1.75 mL)		A, 30 min	>220 ^d	32 min	16	G, 65 °C	1b (3.2/1); 2b (1.8% and 2.0%); 3b (1.7%)
6. 1b (15.7/1)	1.2	Pentane		A, 30 min	254 ^f	0.75 min	0.8	G, 55 °C	1b (14.4/1); 2b (ca. 0.1 and ca. 0.1%); 3b
7. 1b (3.67/1)	2.8	Acetone	Acetone	A, 10 min	305 ^e	3.5 h	28.5	G, 65 °C	1b (1.68/1); 2b (0.2 and 0.3%)
8. ^c 1c	3 μ L/3 mL	Pentane		A, 5 min	254 ^{f,g}	0–3.25 h	0–91.5	I, 190 °C	2c , 3c
9. 1c	7.8	Cyclohexane (2 mL)	Acetophenone (4%)	A, 10 min	305 ^e	80 h	71	E, 160 °C	3c (4.3%)
10. 2c	1 μ L/3 mL	Pentane		A, 5 min	254 ^f	40 min	"High"	I, 190 °C	3c
11. 3c	1 μ L/3 mL	Pentane		A, 5 min	254 ^f	3 h	"Low"	I, 190 °C	None obsd
12. 1d	3.5	<i>n</i> -Hexane		B	254 ^f	565 min	6.6	NMR	None obsd
13. 1d	3.1	Acetone (5 mL)	Acetone	B, 10 min	254 ^f	1100 min	0–98	NMR	3d
14. 1e	4	Acetone (100 mL)	Acetone	A, 30 min	254 ^f	60 h	~90	I, 170 °C	2e (~80%)

^a Procedure A—dry nitrogen bubbled through solution in septum-capped tube; procedure B—argon bubbled through solution in septum capped tube. ^b See Experimental Section for GLC column code. ^c See Figure 6. ^d 450-W medium-pressure Hg lamp with quartz filter. ^e Phosphor coated (305 nm) low-pressure Hg lamp with Pyrex filter. ^f Low-pressure Hg lamp. ^g Merry-go-round apparatus with 254-nm interference filter.

Results

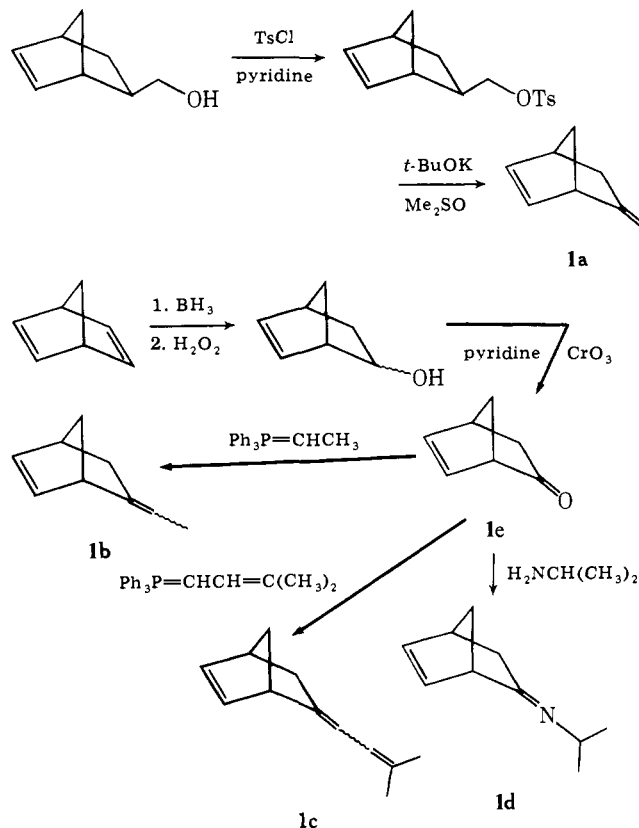
Synthesis of Starting Materials (Scheme I). Elimination from the tosylate of the commercially available bicyclo[2.2.1]hept-2-ene-5-methanol yielded 5-methylenebicyclo[2.2.1]hept-2-ene (**1a**). Bicyclo[2.2.1]hept-2-en-5-one (**1e**) was prepared from norbornadiene by oxidative hydroboration followed by oxidation of the alcohol with chromium trioxide–pyridine. The ketone served as the precursor for 5-ethylidenebicyclo[2.2.1]hept-2-ene (**1b**), 5-(3-methylbut-2-enylidene)bicyclo[2.2.1]hept-2-ene (**1c**), and bicyclo[2.2.1]hept-2-en-5-isopropylimine (**1d**). Appropriate ylides and **1e** yielded **1b** and **1c** and condensation of **1e** with isopropylamine gave **1d**. Each di- π -methane was purified by distillation and/or preparative GLC.

Irradiations. The experimental conditions and results from irradiation of **1a–d** are summarized in Tables I and II and in the Experimental Section.

A. 5-Methylenebicyclo[2.2.1]hept-2-ene (1a). The ultraviolet spectrum of **1a** in cyclohexane solution (Figure 1) showed only tail absorption between 240 nm ($\epsilon < 5$) and 200 nm ($\epsilon 11\,700$). When irradiated in an oxygen-free pentane solution with a 450-W medium-pressure Hg lamp to 50% conversion, **1a** yielded 16% of a photoproduct **2a** and a number of minor products, none of which was a xylene isomer (run 1).⁶ The same conversion of **1a** led to less than 2% of **2a** when acetophenone was employed as a sensitizer.

A sample of **2a** (with 2.5% of **1a**) exhibited a λ_{\max} 210 nm ($\epsilon 11\,800$) as shown in Figure 1. Story⁷ reported λ_{\max} 215 nm for tricyclo[4.1.0.0^{4,7}]hept-2-ene (**4**), and Scott⁸ lists λ_{\max} ~210 nm ($\epsilon \sim 8500$) for substituted vinylcyclopropanes. The infrared spectrum of **2a** contained a 3600 cm^{-1} (s) vinyl C–H stretch, a 3040 cm^{-1} cyclopropane band, a 1665 cm^{-1} (s) C=C stretch, and a 880 cm^{-1} (s) vinyl C–H rocking, all expected from a vinylcyclopropane. The isomeric nature of **1a**

Scheme I

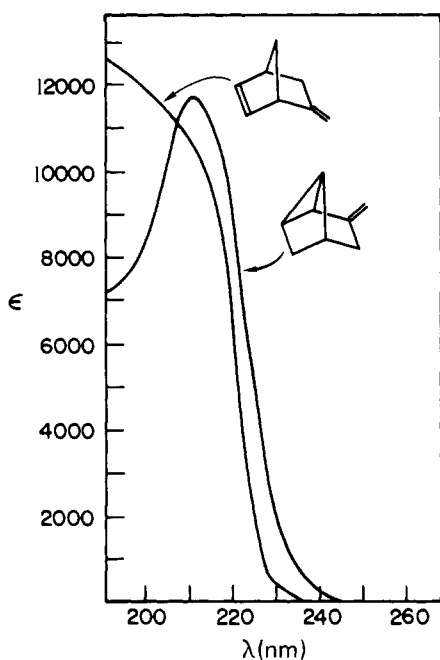


and **2a** was established by mass spectrometry, elemental analysis, and the similarity of their retention times on several GLC columns. Hydrogenation of **2a** over platinum catalyst led

Table II. Actinometry of **1c** Irradiations

Tube	Concn 1c , M × 10 ⁵	Volume, mL	1c , mol × 10 ⁷	Irradiation time, min	Light absorbed, (einsteins/ min × 10 ⁸)	GLC analysis ^a	No. ^b	Solvent	1c conversion, %	Φ _{dis}	Φ _{2c}	Φ _{3c}
15	7.6	4.0	3.05	10.07	1.90	I, 195 °C D, 70–150 °C	4	Pentane ^c	11.2	0.18	0.060	0.066
16	7.6	4.0	3.05	20.29	1.90	I, 195 °C D, 70–150 °C	4	Pentane ^c	22.5	0.18	0.058	0.057
17	7.6	4.0	3.05	30.01	1.90	I, 195 °C D, 70–150 °C	3	Pentane ^c	37.8	0.20	0.048	0.057
18	7.6	4.0	3.05	40.90	1.90	I, 195 °C D, 70–150 °C	4	Pentane ^c	48.9	0.19	0.029	0.037
19	27.8	5.0	13.88	29.92	1.42	J, 100 °C	6	Pentane ^d	6.26	0.20	0.050	0.043
20	27.8	5.0	13.88	29.92	1.42	J, 100 °C	6	Pentane ^d	5.35	0.18	0.049	0.040
21	38.4	5.0	19.2	31.00	1.39	J, 100 °C	5	2-Pro- panol ^d	4.22	0.19		
22	38.4	5.0	19.2	31.00	1.39	J, 110 °C	3	2-Pro- panol ^d	2.89	0.13		
23	38.4	5.0	19.2	52.00	1.39	J, 110 °C	6	2-Pro- panol ^d	5.52	0.15		
24	38.4	5.0	19.2	52.00	1.39	J, 110 °C	6	2-Pro- panol ^d	5.74	0.15		
25	480	5.0	144	135.00	1.39	J, 130 °C	6	2-Pro- panol ^d	1.42	0.15		

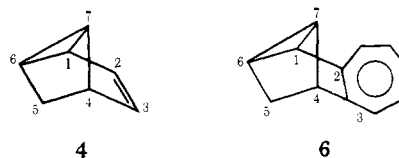
^a See Experimental Section for GLC column code. ^b Number of replicate GLC runs from which the average values for Φ were calculated. ^c Decane as internal standard. ^d Pentadecane as internal standard.

Figure 1. UV spectra of **1a** and **2a** in cyclohexane.

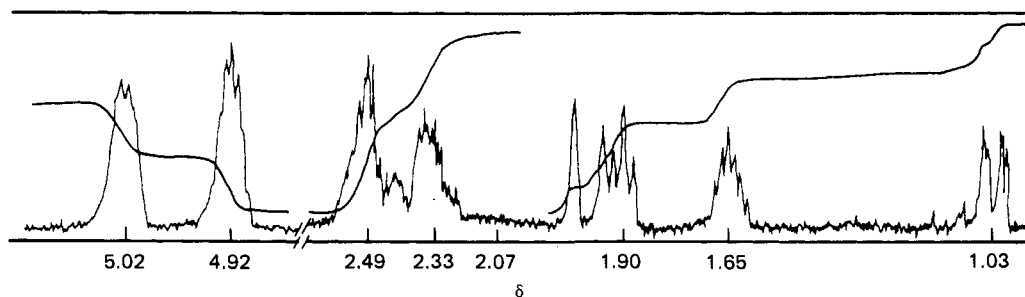
to two compounds, identical in retention times with *endo*- and *exo*-2-methylbicyclo[2.2.1]heptane (**5**). Direct irradiation of **2a** under conditions used in its production from **1a** produced

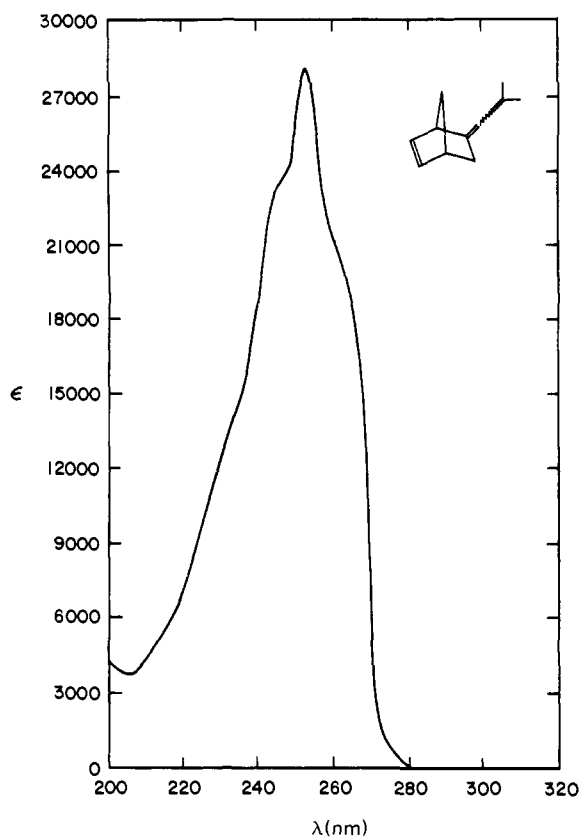
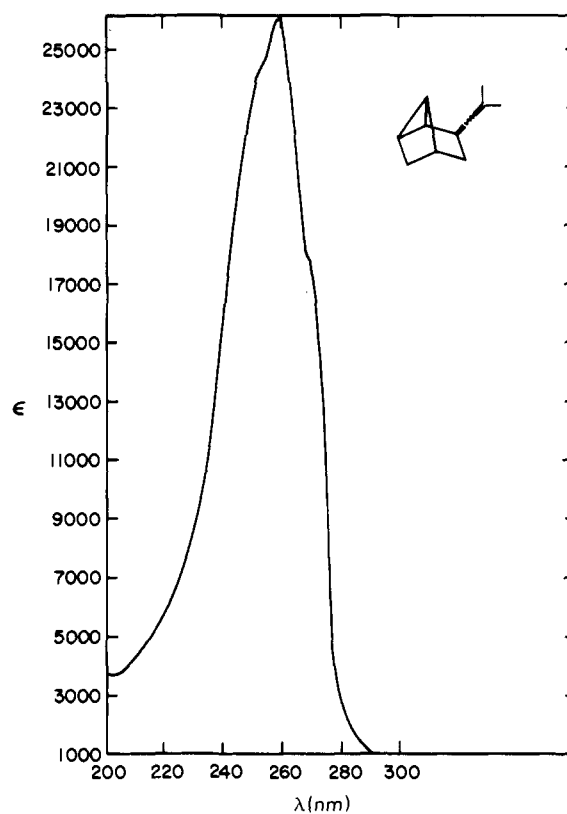
traces of **1a**, several of the minor photoproducts from **1a**, and an unidentified yellow solid.

The structure 2-methylenetricyclo[4.1.0.0^{4,7}]heptane is assigned to **2a** based upon the data above and the similarity of its NMR spectrum (Figure 2) with those of **4**⁷ and **6**.⁹ Story⁷

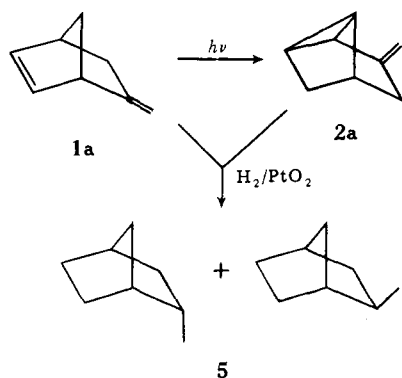


found that the highest field multiplet in the NMR spectrum of **4** is due to H_{5endo}. A multiplet of similar chemical shift (δ 1.03) and shape was found by Edman⁹ in compound **6**. Using this as a base, decoupling experiments allowed assignment of the H₇, H₁, and H₄ signals. Since the main difference between the aliphatic regions of the NMR spectra of **4** and **6** and that of **2a** is an additional AB pattern for the C₃ protons of **2a**, we used Edman's assignments directly to locate some of the other signals. In a benzene solution, the **2a** multiplet of δ 2.33 was separated from the C₃ AB pattern sufficiently so that its major coupling, *J* = 7 Hz, was shown to be different from that of the C₅ endo proton (*J* = 8.5 Hz). Presumably, the C₅ exo proton is placed under the δ 2.49 multiplet with the C₄ proton. This allows the C₆ proton to be assigned to the multiplet centered at δ 2.33. Story found *J*_{4,5endo} ≈ 0 Hz for **4**. Since the dihedral angles for H₄–H_{5endo} and H_{3endo}–H₄ of **2a** are about the same as that of H₄–H_{5endo} of **4**, the H_{3endo} proton of **2a** is assigned

Figure 2. 220-MHz NMR spectrum of **2a** in carbon tetrachloride.

Figure 3. UV spectrum of **1c** in cyclohexane.Figure 4. UV spectrum of **2c** in cyclohexane.

Scheme II



to the high-field unsplit half of the AB pattern centered at δ 2.07. The low-field half due to $H_{3\text{exo}}$ falls in the region of the multiplets at δ 2.3–2.6. The C_8 protons absorb at lower field at δ 5.02 and 4.92.

B. 5-Ethylidenebicyclo[2.2.1]hept-2-ene (1b). Both direct and, to a lesser extent, acetone-sensitized irradiations changed the ratio of stereoisomers of **1b** and produced (as noted in runs 4–7) two isomeric photoproducts (**2b**).¹⁰ The similarity of their structures to **1b** and to each other was indicated by their NMR spectra, obtained with GLC-separated samples. The spectra were nearly identical with each other except for the chemical shifts of the protons of the exocyclic ethylidene: in one isomer, the methyl doublet and broad quartet of the vinyl proton appeared at δ 1.77 and 5.40 respectively; in the other, they were observed at δ 1.72 and 5.30.

When a 94/6 mixture of the **1b** isomers was irradiated with a low-pressure Hg arc to 0.8% conversion (run 6), GLC analysis showed that 0.2% of the **2b** isomers had been produced and in comparable amounts. Since the absorption spectra (and molar extinction coefficients at 254 nm) of the **1b** isomers are nearly identical, the lack of stereospecificity in product for-

mation cannot be attributed to preferential conversion of the minor component in the **1b** mixture. The further change in the ratio of **2b** isomers upon continued irradiation is probably due, in part, to their direct excitation even at low conversions; the molar extinction coefficient of **2b** is significantly larger than that of **1b** at 254 nm.

C. 5-(3-Methylbut-2-enylidene)bicyclo[2.2.1]hept-2-ene (1c). The **1c** stereoisomers could not be separated by GLC on a wide variety of columns, although it was possible to measure their ratio (ca. 1:1) from a 220-MHz NMR spectrum. The ultraviolet spectrum of the mixture in cyclohexane (Figure 3) exhibited λ_{max} 252 nm (ϵ 28 000) and was nearly identical with the sum of the ultraviolet spectra of norbornene and 2-(3-methylbut-2-enylidene)bicyclo[2.2.1]heptane (**7**).

In run 8, direct irradiation of **1c** resulted in its relatively rapid transformation to primarily two photoproducts, **2c** and **3c**. The dependence of the product mixture on percent conversion of **1c** is shown in Figure 6. Acetophenone-sensitized irradiations of **1c** led to its slow disappearance with very inefficient production of **2c**. For example, in run 9, after 71% conversion of **1c**, the sole monomeric product detected was **3c** in 4% yield. The isomeric nature of **2c** and **3c** with **1c** was demonstrated by combined GLC–mass spectrometry. Since both **2c** and **3c** isomerized slowly to other compounds,¹¹ their analyses were performed on freshly isolated samples.

The ultraviolet spectrum of 95% pure¹² **2c**, shown in Figure 4, was similar in shape, position, and intensity to that of **1c**. The presence of the expected infrared peaks and the similarity of the NMR spectrum to that of **2a** served to identify **2c** as the di- π -methane rearrangement product of **1c**. The endo C_5 protons of the **2c** isomers are observed as triplets at δ 0.17 and 0.90. The vinyl region consisted of two broad, overlapping AB patterns with $J \approx 11$ Hz for each. Upon ozonolysis, the sole bicyclic product from **2c** was identical in retention time with **2e**⁵ on four different GLC columns.

From a number of analyses, **3c** was determined to be a mixture of *cis*- and *trans*-3-(3-methylbut-2-enylidene)-5-

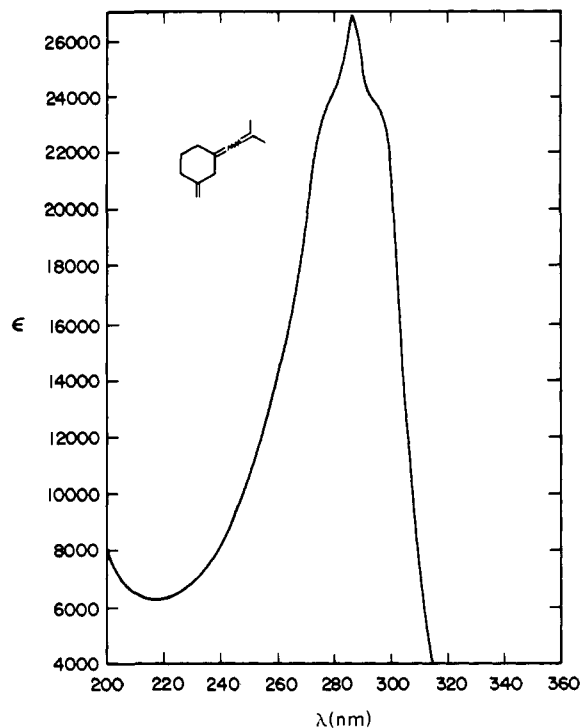


Figure 5. UV spectrum of **3c** in cyclohexane.

methylenecyclohexene. The ultraviolet spectrum of 93% pure¹² **3c** in cyclohexane (Figure 5) displayed λ_{\max} 286 nm (ϵ 26 800), which is incompatible with an acyclic diene. The infrared spectrum of **3c** included a number of peaks between 3000 and 3100 cm^{-1} not present in **1c** or **2c**, a fingerprint region very different from that of **1c**, and a C=C stretching frequency at 1565 cm^{-1} (vs. 1625 cm^{-1} for **1c**). The NMR spectrum of **3c** contained two sets of overlapping doublets (one from each stereoisomer) at $\delta \sim 5.1$. Similar patterns near this chemical shift have been ascribed to exocyclic methylene protons.¹³ The presence of an isobutenyl group in **3c** is indicated by a doublet at δ 1.75. The rest of the high-field part of the spectrum did not resemble those of the tricyclo[4.1.0.0^{4,7}]heptanes. The most notable changes with time in the spectrum of **3c** were the growth of a singlet at δ 1.28, an increase in the relative intensity of the olefinic region, and a decrease in the aliphatic region. The ratio, olefin:methylene:methyl:other aliphatic protons, of a "fresh" sample of **3c** was 4.5:2.0:5.7:3.9. If 4:2:6:4 is the correct "zero-time" ratio, **3c** cannot be bicyclic.

Further evidence for the monocyclic skeleton of **3c** is found in the products (ca. 90% of one compound and 10% of several others) from its hydrogenation over platinum catalyst. Their infrared and NMR spectra were similar to those of an independently synthesized *cis*- and *trans*-3-methyl(3-methylbutyl)cyclohexane mixture (**8**). On four different GLC columns, the major hydrogenation product of **3c** and the major isomer of 3-methyl(3-methylbutyl)cyclohexane had identical retention times.

The two most prominent minor products and **3c** were shown to arise at least partially from secondary photolysis of **2c** (run 10). Neither **2c** nor the above minor products were produced from irradiation of **3c** (run 11).

Gassman's¹⁴ facile conversion of bicyclo[4.1.1.0^{2,7}]heptane to 3-methylenecyclohexene with rhodium dicarbonyl chloride dimer encouraged us to attempt a similar reaction with **2c** since the analogous product would be **3c**. Although the rhodium catalyst dissolved, no change in **2c** was noted after 24 h at 50–55 °C.

The quantum yield for 254 nm light induced disappearance of **1c** in dilute pentane solutions, $\Phi_{\text{dis}} = 0.19$, appeared to be

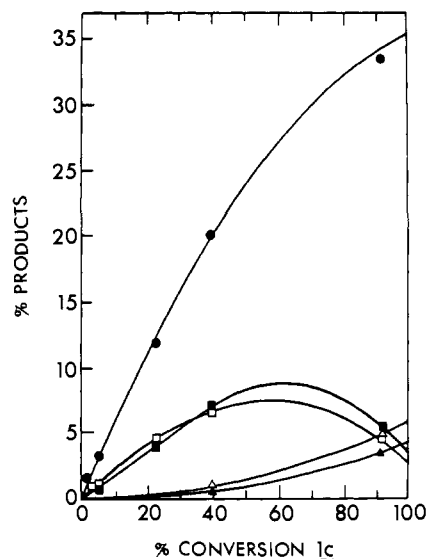
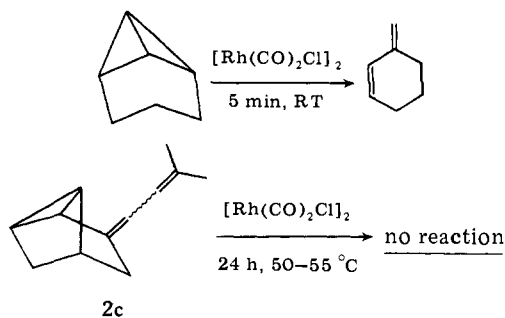


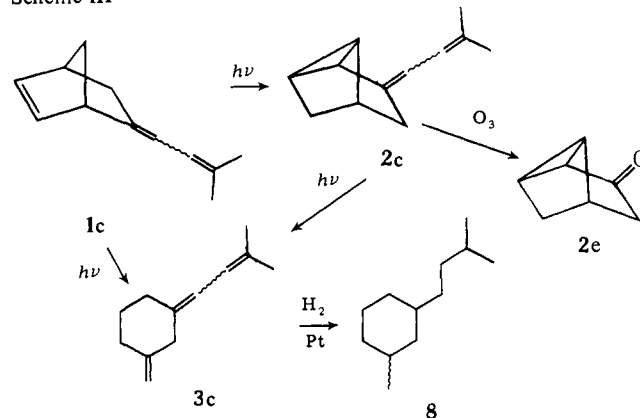
Figure 6. Time dependence of product distribution from irradiation of **1c** (run 8, Table I): **2c** isomers, ■ and □; **3c**, ●; major secondary irradiation products, ▲ and △.

constant to ca. 49% conversion. The quantum yields for production of **2c** and **3c** were not and were therefore extrapolated



to 0% conversion to yield $\Phi_{2c} \approx 0.063$ and $\Phi_{3c} \approx 0.073$. Surprisingly, Φ_{dis} appears to be ca. 25% lower in 2-propanol than in pentane. The data are summarized in Table II.

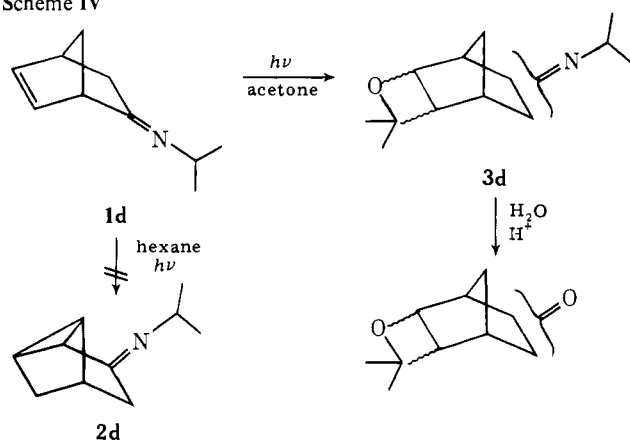
Scheme III



D. Bicyclo[2.2.1]hept-2-en-5-isopropylimine (1d). The imine yellowed quickly upon exposure to air and could be maintained colorless only when stored in the cold under an inert atmosphere. However, no significant differences were observed in the irradiations of yellow and colorless samples. The ultraviolet spectrum of colorless material in cyclohexane showed λ_{\max} 248 nm (ϵ 490) and a tail which extended to about 290 nm ($\epsilon \sim 15$). Unconjugated imines usually exhibit $\lambda_{\max} \sim 240$ nm ($\epsilon \sim 200$) attributed to n, π^* transitions^{15a} and homoconjugated imines are known to display enhanced absorption.^{15b}

Irradiation with 254-nm light of **1d** in *n*-hexane resulted in its very slow disappearance without appearance of any new product having a GLC retention time expected of an isomer (run 12). In acetone solutions, the quantum yield for disappearance of **1d** was ca. 30 times greater than in hexane (run 13). Although no isomeric products were detected, a mixture of oxetanes, **3d**, appeared to be formed.¹⁶ The NMR spectrum of **3d** contained at least three pairs of doublets due to the isopropyl methyl protons (**1d** exhibits three peaks from two partially overlapping doublets for these protons), one broad septet at δ 3.32 from the methine proton of the isopropyl group, and no signal attributable to olefinic protons. A singlet at δ 2.05, not present in **1d**, integrated for six protons. The infrared spectrum of **3d** showed strong imine bands at 1710 and 1670 cm^{-1} ; the imine group of **1d** absorbed at 1690 and 1675 cm^{-1} . The lack of olefinic NMR signals in **3d** was corroborated by the lack of the *cis* olefin peak which appeared at 720 cm^{-1} in the infrared spectrum of **1d**. Acidic hydrolysis of **3d** yielded a new material whose NMR spectrum retained a six-proton singlet at δ 3.35 but neither the doublet nor septet of the isopropyl group. The infrared spectrum of the product displayed one carbonyl peak at 1725 cm^{-1} . The transformations are summarized in Scheme IV.

Scheme IV

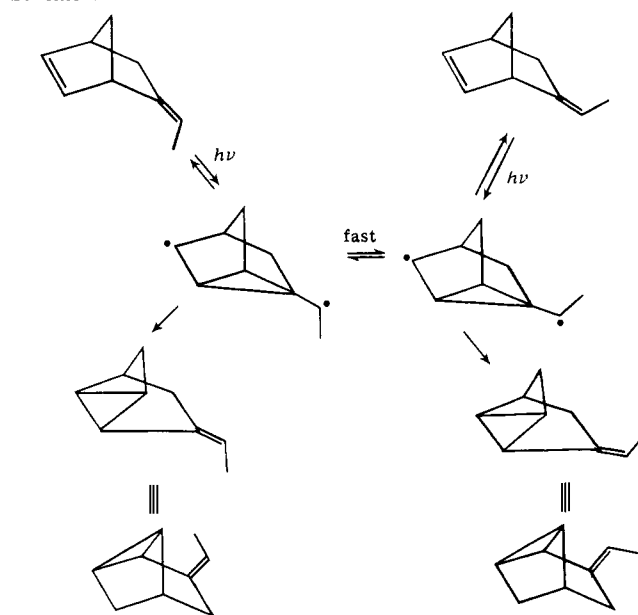


Discussion

There are a number of structural and electronic features of the di- π -methanes **1** which make them mechanistically interesting. (a) They contain only two chromophores, both of which must participate in the reaction.¹⁷ (b) The chromophores are held rigidly within the molecular framework so that their relative orientation is known at all points along the reaction coordinates. (c) The exocyclic chromophore, in all cases, absorbs at least 50% of the light¹⁸ and is capable of dissipating the excitation energy via rotation about its unsaturated bond axis.¹⁹ (d) The geometric constraints of the molecular framework and the nature of the endocyclic chromophore make its arrangement much more attractive energetically than rearrangement of the exocyclic chromophore.²⁰ While some of these features are found in molecules of other studies, it is the simplicity of the system which results when *all* are incorporated that allows a number of the factors governing di- π -methane reactivity to be examined coincidentally.

Nature of the Rearrangement of 1. Both direct and triplet sensitized excitation of **1b** effect both *cis*-*trans* isomerization and skeletal rearrangement. Since the quantum yields are higher for the direct irradiations (see Table I), isomerization reactions must be possible from both excited singlet and triplet states (as long as sensitizer energy transfer occurs with near unit efficiency to **1**). The results show that the exocyclic double bond does not serve as a completely efficient sink for dissipation of electronic excitation energy. Because of the low intensity

of absorption at 254 nm by **1a** and **1b**, it was not feasible to measure absolute quantum yields and the extent of nonproductive decay is not known. Rearrangement of one geometrical isomer of **1b** gave both stereoisomers of **2b** even at low conversion. In contrast, the di- π -methane rearrangement of 1,1-diphenyl-3,3-dimethyl-1,4-hexadiene is highly stereospecific.²¹ These results are entirely consistent with the mechanism shown in Scheme V in which *cis*-*trans* isomerization



ization and skeletal rearrangement arise from a single diradical intermediate. If this mechanism is correct, it is also necessary to postulate that rotation about the newly created exocyclic single bond, which should occur within about 10^{-11} s,²² takes place at about the same rate as rearrangement to a second biradical or products. The mechanism is the same as was suggested by Zimmerman²¹ to account for nonstereospecific rearrangement of triplets in an acyclic di- π -methane.²³

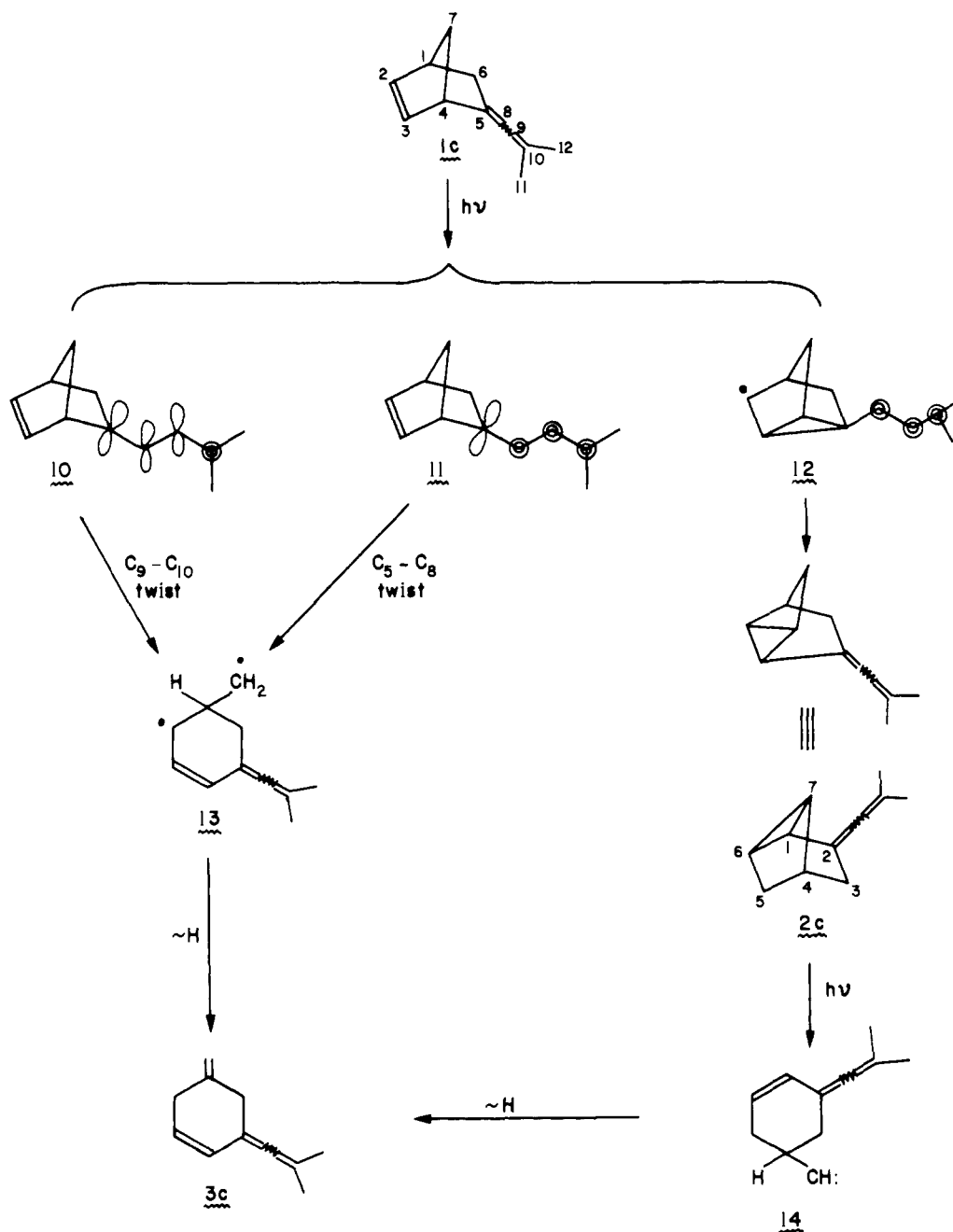
It is of interest to compare the reactivity of **1a** and **1b** with that of **1d** which has a lowest n,π^* singlet. Whereas **1a** and **1b** rearrange efficiently upon direct excitation, **1d** does not. The analogous ketone, **1e**, which also has a lowest n,π^* singlet state, yields bicyclo[3.2.0]hept-2-en-7-one (**9**) via a Norrish type I reaction upon direct irradiation.²⁴ The triplet of **1e** does undergo the di- π -methane rearrangement to yield **2e**.⁵



Attempts to produce triplets of **1d** by sensitization with acetone led only to photoaddition, producing oxetanes. This is the result that would be expected if the triplet excitation energy of **1d** were higher than that of acetone.²⁵ In turn, this implies that the excitation energy of **1d** is higher than that of **1e**,²⁶ a very reasonable possibility in view of the relationship between the n,π^* excitation energies of simple imines and ketones.²⁷ Triplets of **1d** may be formed by intersystem crossing from their excited singlets since nothing is known about the mechanism(s) of nonradiative decay of the latter. If triplets are formed, we would attribute their failure to rearrange to rapid internal conversion involving torsional vibrations of the C=N double bond,^{27,28} a path not available to the ketone.

The rearrangements of **1c** offer an interesting variation from normal di- π -methane reactions. Direct irradiation of **1c** yields

Scheme VI



both **2c** and **3c** as primary products: since Φ_{3c} is greater than Φ_{2c} , the known $2c \rightarrow 3c$ route cannot account for all of the latter product. A suggested mechanism to account for these transformations is given in Scheme VI.

The scheme illustrates our inability to formulate a reasonable mechanism for production of **3c** from both **1c** and **2c** via a common intermediate. The mechanisms do have predictive characteristics which could be tested using isotopic labeling since the exocyclic methylene group of **3c** is derived from different carbon atoms of the original skeleton in the two paths (from C_7 in the $1c \rightarrow 3c$ path and from C_4 in the $2c \rightarrow 3c$ path).

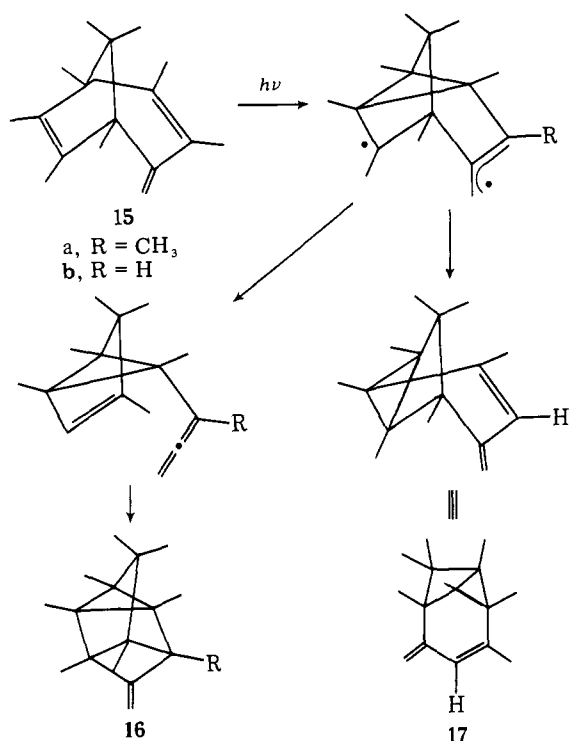
It has been proposed²⁹ that twisted, methylene-allyl configurations are potential minima for both the lowest excited singlet and triplet states of dienes. Consequently we would expect that rapid vibrational relaxation of the excited state of **1c** would produce **10** or **11** (or both), if the endocyclic unsaturated center is not immediately involved. However, the first relaxation process might also produce **12** which would be well on the way to consummation of the di- π -methane rearrange-

ment. Structure **12** can also be visualized as being produced from **11** with less additional geometric distortion than would be required for production of **12** from **10**. Ring opening of either **10** or **11** could produce biradical **13** with a planar heptatrienyl system after rotation about one "single bond" in each case. We have no way of guessing whether or not other minima with twisted configurations would intervene between **10** and **11** and **13**. The cis-trans isomerization which accompanies the two rearrangement reactions is readily accounted for by assuming that **12** is a common intermediate in both geometric isomerization and in the di- π -methane rearrangement. In fact, it is hard to conceive of geometric isomerization occurring without the intermediacy of either **11** or **12** followed by partial decay to the original carbon skeleton.

Photochemical transformation of **2c** to a carbene **14** requires that electronic excitation energy localized mainly in the diene system be converted to vibrational energy in the cyclopropane.^{30a} Other photochemical conversions of cyclopropanes to carbenes are known.³⁰

The photochemistry of **1c** is quite different from that of the

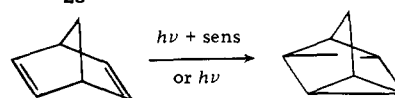
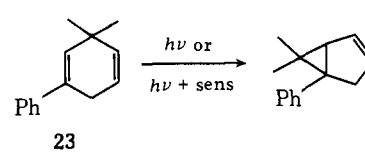
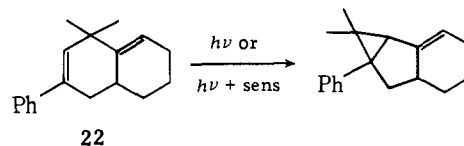
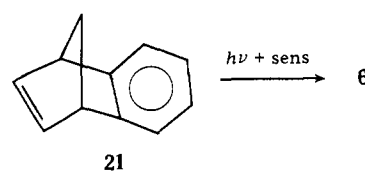
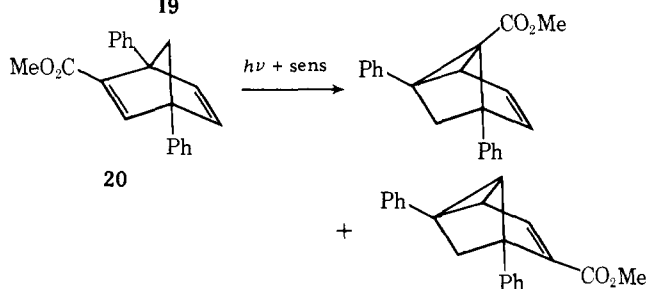
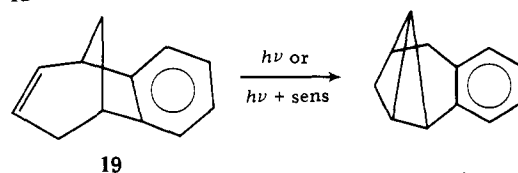
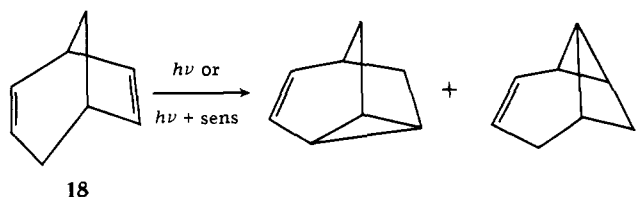
similar di- π -methanes, **15**, investigated by Hart and Kuzuya.³¹ Whereas direct or sensitized irradiation of **15a** produces only the tetracyclic olefin **16a**, **15b** yields **16b** and **17**, the di-



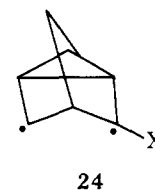
π -methane rearrangement product. Apparently, the tricyclic biradical precursor from **15a** partitions between the di- π -methane pathway and one leading to σ -bond scission and allene formation. The ability of **16** to form from the triplets of **15** while triplets of **1c** yielded **2c** and **3c** very inefficiently is probably a consequence of greater geometric constraint on the diene chromophore of **15**. Whereas the diene in excited **1c** can rotate about its C₅-C₈ or C₉-C₁₀ bonds, free rotation is permitted about only the exocyclic double bond of excited **15**.

Correlation of Reactivity of Di- π -methanes Based on Chromophore Geometry. Burstain^{2b} and Sauer and Shurpik³² have shown that singlets and triplets of bicyclo[3.2.1]octa-2,6-diene (**18**) undergo the di- π -methane rearrangement and similar results have been obtained by Hahn and Rothman³³ for the benzo derivative, **19**. Norbornadiene, however, yields only quadricyclene from direct or sensitized irradiations.³⁴ In fact, of the nonbenzo norbornadienes, only the highly substituted **20** has been found to undergo the di- π -methane rearrangement and, then, only from its triplet state.³⁵ When benzenorbornadiene **21** is irradiated, only its triplet state yields the di- π -methane product.⁹ In a related example, Zimmerman and Tolbert have determined that the di- π -methane rearrangements of either the singlet or triplet of **22** are much more efficient than those of **23** from corresponding states.³⁶

The excited states of norbornadiene and its derivatives can collapse to quadricyclenes with a minimum amount of nuclear motion and, in a number of cases, including the parent compound, simple ring closure takes precedence over the di- π -methane rearrangement where the molecules are promoted to either excited singlet or triplet states. Compounds **20** and **21** do undergo the di- π -methane rearrangement, but exclusively from their triplet states. We doubt that the product of internal cycloaddition of **21** would be thermally stable at room temperature and, therefore, cannot be certain that it is not formed as a part of the decay of the excited state of **21**. The fact that **20** and **21** undergo the di- π -methane rearrangement when excited by triplet sensitizers but not when excited by direct absorption of light may indicate that the triplet state of **21**



probably has a longer lifetime in which to explore vibrational excursions. The fact that norbornadiene itself does not undergo the skeletal rearrangement even with triplet sensitization may indicate a significant role for substituents which would tend to stabilize and prolong the lifetimes of biradical structures such as **24**.



Overall, we can see no new pattern behavior that will be of great help in predicting reactivity in skeletal rearrangements of di- π -methanes in either excited singlet or triplet states. In order to carry out a really meaningful structure-reactivity analysis we would need complete data on the absolute rates of all the excited state relaxation processes, including nonradiative decay to original ground states. For example, we adduce close interlinking between the di- π -methane rearrangements and cis-trans isomerization of compounds **1b** and **1c**. These processes may also be closely related to fast nonradiative decay

mechanisms in which internal conversion puts a good deal of excitation energy into the exocyclic double bonds without leading to detectable rearrangement. Acquisition of data required for believable analysis of the problem will probably have to await development of some suitable subnanosecond kinetic technique.

Experimental Section

The spectrograde solvents employed in the irradiations (acetone, 2-propanol, and benzene, all MCB) were used as received. Pentane, cyclohexane, and 3-methylpentane were purified by the method of Murray and Keller³⁷ and stored in brown glass bottles. Elemental analyses were performed by Spang Microanalytical Labs, Ann Arbor, Mich., and mass spectra were recorded on a Hitachi Perkin-Elmer RMU-6D mass spectrometer at 70 eV by West Coast Technical Service, San Gabriel, Calif. GLC data were recorded on Hewlett-Packard flame ionization gas chromatographs, Models 700 and 5750, and a Varian 90P-3 thermal conductivity gas chromatograph. Columns were 9 ft \times $\frac{3}{8}$ in. 25% β,β -diisopropionitrile and 5% silver nitrate on 60/80 Chromosorb W (A), 10 ft \times $\frac{3}{8}$ in. 20% β,β -diisopropionitrile on 60/80 Chromosorb W (B), 10 ft \times $\frac{1}{8}$ in. 5% SE-30 on 60/80 Chromosorb G (C), 4 ft \times $\frac{1}{8}$ in. 5% Castorwax on 60/80 Chromosorb G(D), 6 ft \times $\frac{1}{8}$ in. 10% UCW 98 on 60/80 Chromosorb W (E), 19 ft \times $\frac{1}{8}$ in. 30% Carbowax 20M on 60/80 Chromosorb W (F), 20 ft \times $\frac{1}{8}$ in. 25% β,β -diisopropionitrile on 60/80 Chromosorb W (G), 10 ft \times $\frac{3}{8}$ in. 20% Carbowax 20M on 60/80 Chromosorb W (H), 10 ft \times $\frac{1}{8}$ in. 30% Carbowax 20M on 60/80 Chromosorb W (I), 6 ft \times $\frac{1}{8}$ in. 10% XF-1150 on 60/80 acid-washed Chromosorb W (J), a 3 ft \times $\frac{1}{8}$ in. 2.5% WF-1 on Porasil D (K), and 5% poly-*m*-phenyl ether on 60/80 Chromosorb W (L). All melting and boiling points are uncorrected.

Bicyclo[2.2.1]hept-2-en-5-one (1e).³⁸ A solution of 184 g (2.0 mol) of norbornadiene and 5.5 g (0.25 mol) of lithium borohydride in 250 mL of anhydrous ether under argon was stirred and cooled at 0 °C. Slowly, 46 g (0.33 mol) of boron trifluoride etherate was added dropwise over 2 h. After 2 h more at 25 °C, the mixture was distilled at room temperature first under aspirator and then under 1 mm of pressure. The remaining residue was diluted with 150 mL of ether and stirred vigorously while 105 mL of 30% sodium hydroxide solution and then, maintaining the pot temperature below 40 °C, 105 mL of 30% hydrogen peroxide were added. After 2 h, the organic layer and an ether extract of the aqueous layer were combined, dried (MgSO₄), and distilled until 78 g of a white sludge remained. This material was oxidized directly with chromic oxide-pyridine by the method of Atkinson et al.^{38b} After being stirred overnight, the reaction mixture was filtered through Celite and the filter cake was washed with 1 L of ether. About 4 L of 30% sulfuric acid-ice was added to the filtrates. Each 2-L portion was extracted with ether (4 \times 150 mL). The combined extracts were washed with water and dried (MgSO₄). Distillation through a 6-in. Vigreux column yielded 34 g (16%) of **1e**, bp 51 °C (12 mm) [lit.³⁹ bp 59.0–59.3 °C (18 mm)]. The carbonyl doublet reported³⁹ to absorb at 1735 and 1725 cm⁻¹ appeared at 1755 and 1740 cm⁻¹ in the infrared spectrum of a neat sample of our **1e**. The NMR spectrum (CCl₄) consisted of signals at δ 6.50 (doublet of doublets, 1 H), 6.05 (doublet of doublets, 1 H), 3.10 (9 lines, 1 H), 2.85 (sextet, 1 H), 2.05 (multiplet, 2 H), and 1.8 (triplet, 2 H).

Bicyclo[2.2.1]hept-2-en-5-isopropylimine (1d). A solution of 0.43 g (4.0 mmol) of **1e** in 5.0 mL of anhydrous ether was added to 12.5 mL of isopropylamine, freshly distilled from potassium hydroxide pellets. Sequentially, 1 drop of trifluoroacetic acid and 2.0 g of flame-dried calcium sulfate were added. The mixture was stirred in the dark at room temperature in a closed vessel for 4.5 days and filtered. The filtrate was distilled to yield 0.36 g (60%) of **1d**, bp 38 °C (0.9 mm). The neat infrared (doublet) imine stretch at 1690 and 1680 cm⁻¹ and other spectral properties of **1d** (vide ante) were consistent with the proposed structure.

5-Methylenebicyclo[2.2.1]hept-2-ene (1a). An ice-chilled solution of 37.2 g (0.3 mol) of bicyclo[2.2.1]hept-2-ene-5-methanol (K and K) in 100 mL of dry pyridine was stirred while 85.8 g (0.45 mol) of *p*-toluenesulfonyl chloride was added. The mixture was sealed, stirred at 0 °C for 1 h, and refrigerated overnight. A 600-mL portion of 10% hydrochloric acid and then 600 mL of water were added slowly. The mixture was extracted with ether (3 \times 200 mL) and the combined extracts were dried (MgSO₄) and evaporated to yield 80 g of sludge, identified by infrared spectroscopy as the desired tosylate.

After stirring at room temperature in a closed vessel for 17 h, a solution of 14 g (50 mmol) of tosylate and 7.33 g (65 mmol) of potassium *tert*-butoxide in 60 mL of dry dimethyl sulfoxide was heated at 110 °C for 1 h. Dilute aqueous carbonate (60 mL) was added and the solution was extracted with pentane (4 \times 100 mL). The pentanes were washed with aqueous bicarbonate, dried (MgSO₄), and distilled carefully through a 10-in. Vigreux column to bp 40 °C. Vacuum distillation of the remaining liquid yielded 2.0 g (38%) of **1a**, bp 55 °C (78 mm) [lit.⁴⁰ bp 67 °C (170 mm)]. The ultraviolet spectrum of **1a** (cyclohexane) displayed $\lambda_{\text{shoulder}} \sim 210$ nm (ϵ 11 000) [lit.⁴¹ $\lambda_{\text{shoulder}}$ 207 nm (isooctane) (ϵ 10 300)]. One of the other fractions, bp 65 °C (4.5 mm), was identified as the *tert*-butyl ether of the starting bicyclic alcohol. In some experiments, commercial **1a** (Aldrich) was employed.

5-Ethylidenebicyclo[2.2.1]hept-2-ene (1b). Under a nitrogen atmosphere, 2.4 g (57 mmol) of a 57% sodium hydride-oil dispersion was added to 200 mL of stirred dimethyl sulfoxide and the mixture was heated at 65–70 °C until all the hydride dissolved. The solution became red as 21.0 g (57 mmol) of ethyltriphenylphosphonium bromide was added to the stirred solution over 5 min. After 1 h of stirring, 5.4 g (50 mmol) of **1e** was added, and the mixture was heated at 60–70 °C for 1 h and cooled. A 500-mL portion of water was added and the liquid was extracted with pentane (4 \times 200 mL). The combined pentanes were washed with 200 mL of water, dried (MgSO₄), and distilled to bp 37 °C. The undistilled portion was purified by GLC on column A (55 °C) and distilled pot-to-pot. GLC analysis on column G (65 °C) indicated the presence of both stereoisomers of **1b** in a 62/38 ratio.⁴² In some experiments, commercial **1b** (Union Carbide) of different isomeric ratio was employed.

5-(3-Methylbut-2-enylidene)bicyclo[2.2.1]hept-2-ene (1c). The method above, using 3-methyl-2-butenyltriphenylphosphonium chloride as the ylide precursor, was employed to synthesize **1c**, bp 60 °C (1.0 mm), in 60% yield. After vacuum distillation, **1c** was purified further by preparative GLC on column H (190 °C) and pot-to-pot vacuum distillation. Only one peak was observed in the GLC traces employing columns H (190 °C) and J (120 °C). Combined mass spectrometry-GLC (column J, 120 °C) analysis of **1c** showed a parent peak at *m/e* 160 (P + 1, 3.4%; P + 2, 1.6%) and a base peak at *m/e* 79. The NMR spectrum of **1c** (CCl₄) was complex and indicated the presence of two stereoisomers in about equal concentrations. An AB pattern (*J* \approx 12 Hz), integrating for ca. one proton, with the low-field portion buried under another resonance and the high-field peaks split into septets, was centered at δ 5.85. The other resonances were at δ 6.0 (multiplet, 3 H), 3.55 (broad, $\frac{1}{2}$ H), 3.1 (multiplet, $\frac{1}{2}$ H), 2.95 (broad, 1 H), and a series of small peaks with a large, unsymmetrical doublet centered near δ 1.7 (\sim 10 H).

Hydrogenation of 1a. A 5-g portion of **1a** in 70 mL of pentane was reduced on a Parr shaker with hydrogen using 0.2 g of 10% Pd/C as catalyst. The mixture was filtered through diatomaceous earth and the filtrate was distilled. A 3-g center cut of *endo*- and *exo*-2-methylbicyclo[2.2.1]heptane (**5**),⁴³ bp 125 °C (lit.⁴⁴ bp 127 °C), was collected.

Synthesis of 3-Methyl(3-methylbutyl)cyclohexane (8). A stream of nitrogen was blown over 250 mL of stirred, dry benzene for 5 min before 11.0 mL of 2 M phenyllithium in 70:30 benzene-ether was added. (3-Methylbut-2-enyl)triphenylphosphonium chloride (7.4 g, 20 mmol) was added slowly and the mixture was refluxed and stirred under nitrogen for 30 min. 3-Methylcyclohexanone (6.72 g, 60 mmol) was dripped in and the reflux was continued for 3 h. After standing overnight, the mixture was filtered and eluted with pentane on a 30-g column of alumina. A 3-g fraction, bp 77–109 °C (23–20 mm), was used in the subsequent reaction.

About 2 g of the above material in 20 mL of benzene was reduced under a hydrogen atmosphere with platinum oxide catalyst. After being passed through diatomaceous earth, the filtrate was reduced to ca. 2 mL on a rotary evaporator and eluted through a 50-g column of alumina with pentane. The 25–50 mL fraction contained ca. 1.5 g of the desired product, as determined by infrared and ultraviolet spectroscopy. Two peaks (cis and trans isomers) were observed by GLC on columns J (50 °C), K (70 °C), and L (80 °C).

Preparation of 2a.⁴⁵ A solution of 5.0 g of **1a** (Aldrich, distilled from lithium aluminum hydride) in 250 mL of pentane was irradiated for 4 days under nitrogen with a 450-W medium-pressure mercury arc lamp immersed in a quartz well. The liquid was filtered and distilled carefully to bp 36 °C through a 12-in. Vigreux column. The **2a** in the remaining liquid was purified by GLC twice on column H (75 °C) and

distilled pot-to-pot. The second injection yielded **2a** containing 2.5% **1a**. A 220-MHz NMR spectrum of **2a** (CCl_4) is shown in Figure 2. An NMR spectrum (60 MHz) in benzene consisted of peaks at δ 5.15 (finely split doublet, 2 H), 2.1–2.65 (multiplet, 4 H), 2.0 (singlet, 1 H), 1.8 (doublet, 1 H), 1.5 (sextet, 1 H), and 1.05 (doublet of doublets, 1 H).

Anal. Calcd for C_8H_{10} (**2a**): C, 90.57; H, 9.43. Found: C, 90.34; H, 9.44.

Hydrogenation of 2a. Nitrogen was passed for 5 min over a stirred mixture of 2.5 mL of benzene and 50 mg of platinum oxide in a closed test tube (except for gas inlet and outlet). The tube was cooled in a cold water bath, 50 mg of **2a** was added via syringe, and hydrogen was bubbled through the liquid for 75 min. The filtered liquid was distilled to bp 85 °C. The two nonbenzene peaks of the liquid residue were found by GLC on column F (110 °C) to have the same retention times as **5**.

Preparative Irradiation of 1c. Nitrogen was bubbled through a solution of 1 g of **1c** in 100 mL of pentane for 30 min. Bubbling was continued while the solution was irradiated for 16 h with a low-pressure mercury arc immersed in a quartz well. The liquid of bp >70 °C was separated by preparative GLC on column H (200 °C). The first peak, **1c**, and the second, **3c**, were collected separately. The third and fourth peaks, **2c**, were collected together. A series of other, minor peaks were noted at retention times near those of **1c**, **2c**, and **3c**. Each sample was distilled pot-to-pot before being analyzed.

A combined mass spectrometry–GLC (column J, 120 °C) analysis of the filtered reaction liquid was performed. The **2c** displayed a parent ion at m/e 160 ($P + 1$, 14.0%; $P + 2$, 1.0%) as did **3c** ($P + 1$, 14.8%; $P + 2$, 1.4%). In addition, the mass spectra of four minor products also displayed parent ions at m/e 160. One minor product with an apparent parent ion m/e 162 ($P + 1$, 14.8%, $P - 1$, 11.1%; $P - 2$, 55.6%) appeared to be partially reduced and two others with parent ions at m/e 176 ($P + 1$, 19.5 and 17.9%), at least formally, are products of addition between a compound isomeric with **1c** and methane.

Ozonolysis of 2c.⁴⁶ A stream of ozone from a T-408 Welsbach ozonator was scrubbed with sulfuric acid, passed through a tower of anhydrous calcium sulfate, and bubbled through a solution of 75 mg of **2c** and 73 mg of pyridine in 4 mL of chloroform maintained at –10 °C. The reaction was stopped after 15 min when the exiting gas discolored aqueous potassium iodide. By GLC analysis on columns C (85 °C) and I (170 °C), no **2c** remained. In its place, solvent and one peak with the same retention time (separate and coinjection) as **2e**, produced from **1c** via the method of Ipaktschi,⁵ appeared.

Attempted Rearrangements of 2c and 2e with Rhodium Dicarbonyl Chloride Dimer. About 25 mg of **2c**, 2.3 mg (7% molar equivalent of **2c**) of rhodium dimer, and 0.3 mL of deuteriochloroform were shaken in one closed NMR tube and 65 mg of **2e**, 4.0 mg of dimer (3.5% molar equivalent of **2e**), and 0.9 mL of deuteriochloroform were shaken in another. As the rhodium complex dissolved, the **2c** and **2e** solutions became dark yellow and yellow, respectively. Both tubes were heated for 24 h at 50–55 °C and showed no reaction by NMR and GLC (column I, 200 °C) analyses.

Hydrogenation of 3c. Hydrogen was bubbled through a mixture of 10 mg of platinum oxide and 2 mL of benzene for 10 min before adding 10 mg of **3c**. The mixture was stirred and hydrogen bubbling was continued for 2 h. After filtration through diatomaceous earth and distillation until ca. 50 mg remained, the residual liquid was analyzed by GLC on columns I (80 °C), J (50 °C), K (70 °C), and L (80 °C). The retention times (separate and coinjections) of the residue and the major isomer of 3-methyl(3-methylbutyl)cyclohexane were found to be the same in all cases.

Preparation and Hydrolysis of 3d. Argon was bubbled through a solution of 23 mg of **1d** in 5.0 mL of acetone in a Pyrex tube for 10 min. The tube was sealed and placed next to a Pyrex well with a 450-W medium-pressure mercury arc for 18 h. After removal of solvent, the residue was taken up in 0.3 mL of deuteriochloroform. By NMR and GLC analyses (column E, 120 °C), **3d** and ca. 2% of **1d** were the only compounds present.

The chloroform solution was shaken vigorously with ca. 1 mL of dilute hydrochloric acid for 30 min and dried (MgSO_4). The NMR and infrared spectral evidence for the nature of the product included the absence of a six-proton high-field doublet (indicative of the isopropyl group in **1d**), and the presence of a six-proton singlet at δ 3.45 and a carbonyl stretch at 1725 cm^{-1} .

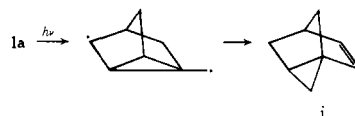
Quantum Yield Determinations (Table II). Solutions of freshly distilled **1c** containing a saturated hydrocarbon as internal standard were

prepared in sufficient concentrations to absorb essentially all of the light at 254 nm ($\text{OD} > 3$). Measured aliquots were pipetted into clean and dry matched quartz tubes which were then degassed by three freeze–pump–thaw cycles (7×10^{-4} Torr) and sealed on a mercury-free vacuum line. The tubes were irradiated on a 254-nm merry-go-round apparatus.⁴⁷ Duplicate actinometry by the method of Parker and Hatchard⁴⁸ was performed immediately prior to irradiations. After being irradiated, the tubes were opened and their contents analyzed by GLC. The unirradiated stock solution served as a zero irradiation time standard. The GLC peaks were weighed on a Mettler balance. The ratio of (product/standard)_{time=t} to (**1c**/standard)_{time=0} gave the chemical yields. Quantum yields were determined by multiplying the chemical yields by the number of moles of **1c** in each tube and then dividing by the total number of einsteins absorbed by the tube. Multiple GLC traces were recorded for each tube and the numbers were averaged.

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- (11) In addition, GLC-purified samples of **3c** yellowed when stored regardless of precautions to keep them dark, dry, cold, and anaerobic.
- (12) The contaminants in the GLC-isolated samples of **2c** and **3c** were **1c**, **2c**, and **3c**. Since the spectra of pure **1c** and nearly pure **2c** and **3c** are known, it is possible to state that the effects of a small amount of any one compound on the ultraviolet spectrum of another must be negligible.
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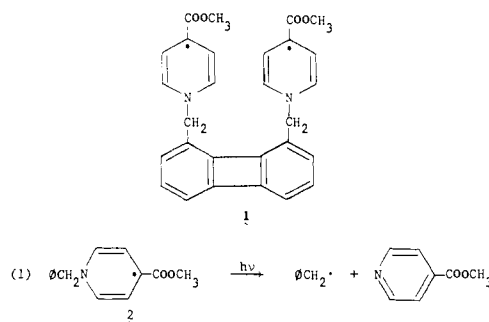
Stable Free Radicals. 8. Photochemical Decomposition of 1,8-Biphenylenediyl Bismethyl and *o*-Xylenyl Pyridinyl Diradicals

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Abstract: The photosensitivity of 1-benzyl-4-carbomethoxypyridinyl radicals has been found also in the pyridinyl diradicals, 1,8-biphenylenediyl bismethyl and *o*-xylenyl, and their magnesium complexes. In neither series is the quantum yield of decomposition especially high. Irradiation in the visible absorption band does not cause photodecomposition, but does apparently favor the formation of the most highly absorbing magnesium complexes. Irradiation in the first strong absorption band of the radical (near 400 nm) is more effective than irradiation in the short wavelength absorption band (260 nm) for causing photodecomposition. A specific synthesis for 1,8-dimethylbiphenylene has been developed.

In the course of investigations designed to study the properties of pyridinyl diradicals with specified distances separating the pyridinyl radical moieties, we experienced difficulty in generating and retaining a 1,8-biphenylenediyl bismethyl pyridinyl (**1**). A possible reason for this unexpected result became apparent only after we learned of the discovery of Ikegami and Watanabe^{2a,b} that 1-benzyl-4-carbomethoxypyridinyl (**2**) was rather photosensitive, decomposing to methyl isonicotinate and the benzyl radical (eq 1). With proper precautions against exposure to light, we then successfully prepared diradical **1**. In order to establish conditions for the use of diradicals like **1** in other experiments, and to obtain further information on the novel process of photodecomposition of stable free radicals, we have made a study of the photolysis of two pyridinyl diradicals and their magnesium complexes. We here report the results, together with a synthesis developed for the specific preparation of 1,8-biphenylene.



Results

Synthesis of 1,8-Dimethylbiphenylene. The usual synthesis of biphenylene derivatives via benzyne intermediates leads to