Photoisomerization of Bicyclo[3.2.1]octadiene[1]

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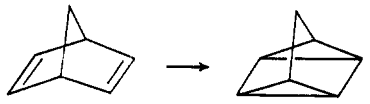
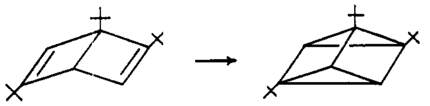
Light-induced isomerizations of bicyclo[3.2.1]octadiene have been investigated. Under a variety of conditions a mixture of tricyclo[3.2.1.$0^{2,7}$]oct-3-ene (**6**) and tricyclo[5.1.0.$0^{5,8}$]oct-2-ene (**7**) was obtained. Intramolecularity was demonstrated by a labeling experiment. Possible mechanisms for the transformations are discussed.

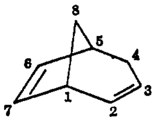
Light-induced transformations of olefinic systems have been the subject of intensive synthetic and mechanistic studies.[2] The unique ability of photochemical processes to produce highly strained systems is a particularly fascinating aspect of this subject.

In this connection, the photocycloadditions of norbornadienes,[3] **1** → **2**, and Dewar benzenes,[4] **3** → **4**, provide striking examples.


1 **2**


3 **4**

Although these systems are not formally conjugated, it is clear from their ultraviolet spectra[3,4] that interactions of the π systems in the excited states are significant.[5] In this connection it was of considerable interest to investigate a homolog of norbornadiene, namely bicyclo[3.2.1]octadiene (**5**). In this system the degree of bonding in the excited state would be expected to be diminished owing to the greater separation of the pair of carbon atoms at the ends of the chromophores (*i.e.*, carbons 3 and 6).



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Results

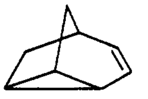
In agreement with the above discussion, the ultraviolet spectrum of **5** revealed none of the fine structure[5] associated with the spectrum of **1**; instead, only end absorption was observed. This observation does not preclude 3,6 interaction, but rather it reflects on the magnitude of such overlap.

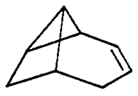
Photolyses of **5** were carried out under a variety of conditions including direct irradiation in cyclohexane, mercury vapor sensitized excitation, and ketone-sensitized excitation. In general, two photoisomers, A and B, were produced in varying ratios; the results are summarized in Table I.

TABLE I
PHOTOISOMERIZATION OF 5

Irradiation	λ, Å	Ratio of A:B
Acetone sensitized	>2600	4:1
Acetophenone sensitized in C_6H_{12}	>2900	4:1
Mercury vapor sensitized	2537	1:45:1
Direct in C_6H_{12}	2537	1:4

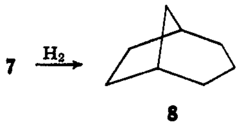
At this time, the major considerations dealt with the structures of photoproducts A and B. Nuclear magnetic resonances and infrared spectral data revealed that both isomers were unsaturated tricyclic systems. From mechanistic considerations (see below) the two most reasonable structures for A and B appeared to be **6** and **7**, respectively.


6 (A)


7 (B)

Compound **6** had been reported earlier by von Doering and Grob and their coworkers[6] and a sample was available from a previous study.[7] The two samples proved to have identical spectra.

The structure of B was confirmed on the basis of its ready reduction to bicyclo[3.2.1]octane **8** and the



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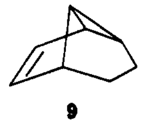
observation of an ultraviolet absorption maximum at *ca.* 205 mμ (ε 5400) indicative of a vinylcyclopropane system.[8] This datum and the nmr spectrum clearly distinguish this compound from the closely related isomer tricyclo[5.1.0.$0^{4,8}$]oct-2-ene (**9**).[8]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Discussion

Speculations as to the origin of the photoproducts **6** and **7** will be discussed in terms of the possible

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[1] Presented at the Second Middle Atlantic Regional Meeting of the American Chemical Society, New York, N. Y., Feb 1967, Abstracts, p 68.

[2] For recent reviews, see (a) R. O. Kan, "Organic Photochemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, Chapter 2, and (b) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, Chapter 4.

[3] S. J. Cristol and R. L. Snell, *J. Am. Chem. Soc.*, **80**, 1950 (1958); W. G. Dauben and R. L. Cargill, *Tetrahedron*, **15**, 197 (1961); G. S. Hammond, N. J. Turro, and A. Fischer, *J. Am. Chem. Soc.*, **83**, 4674 (1961).

[4] K. E. Wilzbach and L. Kaplan, *ibid.*, **87**, 4004 (1965); D. M. Lemal and J. P. Lokensgard, *ibid.*, **88**, 5934 (1966); W. Schäfer, R. Criegee, R. Askani, and H. Grüner, *Angew. Chem.*, **79**, 54 (1967).

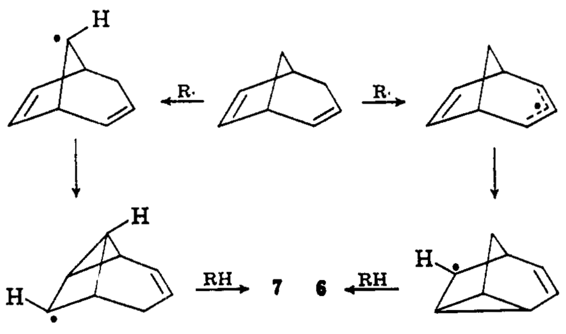
[5] C. F. Wilcox, Jr., S. Winstein, and W. G. McMillan, *J. Am. Chem. Soc.*, **82**, 5450 (1960).

[6] W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963); C. A. Grob and J. Hostynek, *Helv. Chim. Acta*, **46**, 1676 (1963).

[7] R. R. Sauers, J. A. Beisler, and H. Feilich, *J. Org. Chem.*, **32**, 569 (1967).

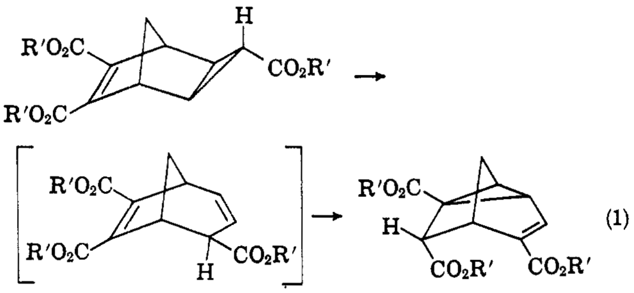
[8] See O. L. Chapman, G. W. Borden, R. W. King, and B. Winkler, *J. Am. Chem. Soc.*, **86**, 2660 (1964), for examples.

SCHEME A



atomic rearrangements involved and the nature of the excited states which may be responsible for these changes.

Three basic mechanistic pathways have been considered as reasonable possibilities in the present system. The first of these (Scheme A) involves hydrogen abstraction followed by cyclization and readdition of hydrogen. This type of mechanism has been postulated to account for the thermal conversion of tricyclo-[3.2.1.0^{2,4}]octenes into tricyclo[3.2.1.0^{2,7}]octenes.[9]



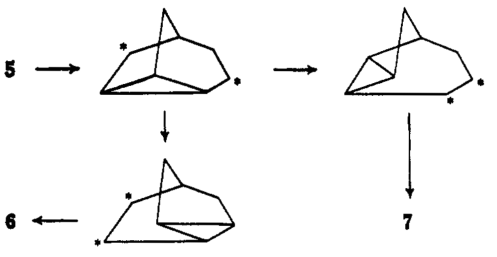
(1)

In eq 1, R· could be the triplet carbonyl group or adventitious traces of radicals. RH could be compound **5** or solvent molecules.[10] These over-all changes could occur intramolecularly as well by 1,3 shifts of hydrogen with concurrent rebonding.[11]

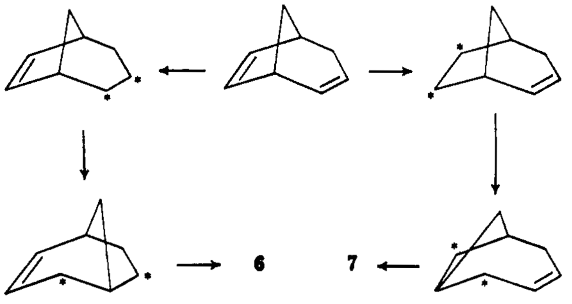
Mechanistic Scheme B is patterned after the sequences proposed by Zimmerman and Chapman[12] for photoisomerizations of dienones. Excitation effects 2,7 bonding which is followed by cyclopropylcarbinyl rearrangements and, ultimately, product formation.[13]

Finally, an alkyl migration process may be involved as formalized in Scheme C. For the sake of clarity, the two double bonds are viewed as being independent of one another. Good analogy for this type of rearrangement has been provided by Kristinsson and Griffin in the photorearrangements of simple olefins.[14]

SCHEME B

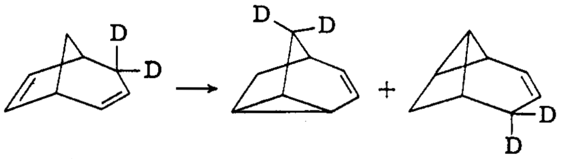


SCHEME C



A study of the isotopic changes associated with the photolysis of 4,4-dideuteriobicyclo[3.2.1]octadiene (**5**-d_2)[15] appeared to be a fruitful experimental approach to provide information concerning the above mechanisms. Only Scheme A would be expected to involve scrambling or exchange of deuterium.

Experimentally, it was found that both products of this reaction retained essentially all of the original deuterium. Furthermore, from analysis of the effects of the isotope on the nmr spectra, it is clear that the CD_2 group was still intact in both products.[16] Thus,



5-d_2 **6**-d_2 **7**-d_2

at least **6** cannot be formed *via* a radical abstraction mechanism. This being the case, it seems unlikely that **7** would be so formed either, since it would be difficult to rationalize attack at C-8 in preference to the allylic position at C-4.

With respect to the excited states involved, it seems safe to conclude that triplet states are involved in the sensitized experiments. Since norbornene[17] and cy-

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[9] H. Prinzbach, W. Eberbach, M. Klaus, G. v. Veh, and U. Scheidegger, *Tetrahedron Letters*, 1681 (1966).

[10] For another analogy, see J. E. Baldwin and R. H. Greeley, *J. Am. Chem. Soc.*, **87**, 4514 (1965); *cf.* I. Haller and R. Srinivasan, *ibid.*, **88**, 5084 (1966).

[11] For examples, of 1,3-hydrogen shifts in photochemical rearrangements, see W. G. Dauben and W. T. Wipke, *Pure Appl. Chem.*, **9**, 539 (1964); 1,3-hydrogen shifts may also be involved in the formation of phenylindan from diphenylcyclopropane reported by G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson, and G. Klose, *J. Am. Chem., Soc.*, **87**, 1410 (1965).

[12] H. E. Zimmerman and O. L. Chapman in "Advances in Photochemistry," Vol. I, W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr., Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp 183, 323.

[13] It is not known to what degree these processes may be concerted or what other intermediate stages may be involved. It is also conceivable that the ring-closed product i is involved as a vibrationally excited species.

i

For a possible analogy, see J. N. Pitts, Jr., L. D. Hess, E. J. Baum, E. A. Schuck, J. K. S. Wan, P. A. Leermakers, and G. Vesley, *Photochem. Photobiol.*, **4**, 305 (1965).

[14] H. Kristinsson and G. W. Griffin, *J. Am. Chem. Soc.*, **88**, 378 (1966).

[15] J. M. Brown and J. L. Occolowitz, *Chem. Commun.*, 376 (1965).

[16] Experimentally the product **6**-d_2 still displayed resonance peaks attributable to a CH_2 grouping as evidenced by the appearance of an unsymmetrical doublet (J = 11 cps) centered at τ 9.33. The same multiplet appeared in the spectrum of **6**, but with twice the relative area. A CHD grouping would be expected to give rise to a singlet or a closely spaced doublet. In the spectrum of **7**-d_2, the adjacency of the CD_2 group to the double bond was readily apparent from the marked simplification of the absorptions of the latter. A *ca.* twelve-line multiplet was seen in the vinyl region of the spectrum of **7**. In the spectrum of the deuterated analog, a six-line multiplet was observed which consists of the AB portion of an ABX spin system in which J_{AB} = 11 cps, $J_{BX} \sim 5$ cps, and $J_{AX} \sim 0$ cps.

[17] H. D. Scharf and F. Korte, *Tetrahedron Letters*, 821 (1963); D. R. Arnold, D. J. Trecker, and E. B. Whipple, *J. Am. Chem. Soc.*, **87**, 2596 (1965).

clopentene[18] have been caused to dimerize in photosensitized reactions, there is no reason to doubt that energy transfer is the initial step here, also. Since direct irradiation generates the same products, albeit in a different ratio, it appears that singlet states may be involved in the photoisomerization.[19] In the mercury-sensitized experiment, one also sees a change[19] in the product ratio. In this case, higher vibrational (triplet) levels may be involved, since the reaction was carried out in the gas phase. In any case, an unambiguous decision as to the required excited state(s) cannot be made with the available data.

The major significance of these results are in the implications that rearrangements of 1,4-dienes are general even in the absence of special features, *e.g.*, aromatic rings.[14,20] or other unusual structural features as are present in barrelene.[21] Mercury-photosensitized reactions of 1,4-dienes in the vapor phase have recently been shown to yield vinylcyclopropanes in further support of this generalization.[22] Of course, it remains to be demonstrated that the mechanisms of these diverse reactions follow similar paths.

Experimental Section

Analyses were done by Micro-Tech Labs, Skokie, Ill. Infrared spectra were determined in carbon tetrachloride or as noted on either Beckman Model 5A or Perkin-Elmer Model 21 spectrophotometers. Nuclear magnetic resonance data were obtained on a Varian Model A-60 spectrometer in carbon tetrachloride. Gas chromatograms were determined on an Aerograph Model A90P on 0.25-in. columns or on a Barber-Colman Model 5000 flame ionization instrument in the cases of capillary chromatograms. Melting points were determined on a Mel-Temp apparatus and are uncorrected.

Bicyclo[3.2.1]octadiene (5) was prepared according to the procedure of ref 23 and had bp 124–125° (lit.[23] bp 121°). The nmr spectrum agreed with the description given.[23]

The ultraviolet spectrum showed only end absorption in methanol. The following values of ε at various wavelengths serve to characterize this spectrum: <10 (250 mμ), 134 (235 mμ), 380 (230 mμ), 1220 (220 mμ), and 2040 (210 mμ).

4,4-Dideuteriobicyclo[3.2.1]octadiene (5-d_2) was prepared similarly except that trideuteriomethyl bromide (99%) was used to prepare the Wittig reagent. A 45% yield of **5**-d_2 was obtained, bp 122°. The nmr spectrum displayed four olefinic protons at τ 3.83 (q), 4.09 (d), 4.38 (q), and 4.88 (d). A broad peak appeared at τ 7.34 (2 H) and complex absorption between τ 7.88 and 8.47 accounted for the remaining protons. The absorption at 7.8 in **5** was essentially absent in the deuterated system. The infrared spectrum of **5**-d_2 showed peaks attributable to CD stretching modes at 4.64, 4.71, and 4.82 μ. Other peaks appeared at 9.43, 9.65, 9.87, 10.17, 10.49, 10.78, 10.99, 11.5 (s), 14.06 (vs), and 15.2 μ (vs).

Photolysis of 5 in Acetone.—Typical photolyses of **5** were carried out on 0.5–1% solutions in spectrograde acetone. The apparatus consisted of a quartz immersion well with a Corex filter and a 200-w Hanovia medium-pressure mercury lamp. The reaction flask required about 600 ml of solvent and was purged with nitrogen during the irradiation. Aliquots were removed during the runs and were analyzed by gas chromatography on a 12-ft column of Apiezon L at 110°. Two new components gradually appeared as the starting material reacted. The ratio of the new products was essentially constant at 4:1 up to the point (60 hr) at which the reaction was ceased. At this time, about 88% of the starting material had disappeared and the total area of the product peaks amounted to 45% of the starting peak. On prolonged irradiation, the yield of product dropped off markedly. At this point, the solvents were carefully distilled through a spinning-band column (18 in. × 6 mm). The last traces of solvent were removed by distillation at 0.1 mm and room temperature, the volatile products being collected in a receiver cooled in a Dry Ice bath. The two photoisomers were purified by gas chromatography.

The major product (36%) showed an infrared spectrum which agreed with the literature data for **6**. The nmr spectrum displayed a triplet at τ 4.26 (2 H), a quintuplet at 7.58 (1 H), complex absorption between 8.25 and 8.80, and an unsymmetrical doublet (J = 11 cps) centered at 9.30 (2 H).

The minor photoproduct (9%) exhibited an infrared spectrum with bands at 3.32 (s), 3.44 (s), 6.13 (w), 7.92, 11.47, 12.00, 13.95, and 15.20 μ (s). The nmr spectrum showed a complex multiplet centered at τ 4.3 (2 H) and complex absorption between 7.2 and 9.0 (8 H).

The ultraviolet spectrum showed maximum absorption at 205 mμ (ε 5400) in methanol. These data differ significantly from those reported for tricyclo[5.1.0.0^{4,8}]oct-2-ene[8] and the preferred structure for this product is that of tricyclo[5.1.0.0^{5,8}]-oct-2-ene (**7**).

Reduction of Tricyclo[5.1.0.0^{5,8}]oct-2-ene.—A solution of 0.106 g (1.0 mmole) of **7** in 10 ml of ether was added to a mixture of 0.015 g of prereduced palladium on charcoal (10%) and 4 ml of ether. A total of 47.9 ml of hydrogen was absorbed (theory: 49.2 ml).

Addition of Filter-Cel was followed by filtration of the reaction mixture. The ether was distilled through a spinning-band column and the residue was analyzed by gas chromatography on a 150 ft × 0.01 in. column of Apiezon L (82°). Three products were observed in the area ratios 1:7:2. The major peak coincided in retention time with that of a sample of bicyclo[3.2.1]octane prepared by catalytic reduction[23] of **5**. The component present to the extent of 10% had a retention time identical with that of a sample of bicyclo[4.2.0]octane.[24] Preparative-scale gas chromatography allowed isolation of the major component. Its identity with bicyclo[3.2.1]octane was established by comparison of infrared and nmr spectra with those of an authentic sample.[23]

Photolyses of 4,4-Dideuteriobicyclo[3.2.1]octadiene (5-d_2).—A solution of 3 g of **5**-d_2 in 600 ml of acetone was irradiated as described above. The starting diene and the two deuterated products were isolated and subjected to nmr and mass spectral analysis.

The nmr of the recovered diene was essentially identical with that of the starting material. The nmr spectrum of the dideuterated olefin **6**-d_2 showed a triplet at τ 4.23 (2 H), a broad quartet at 7.58 (1 H), complex absorption between 8.30 and 8.85 (4 H), and an unsymmetrical doublet (J = 11 cps) centered at 9.32 (1 H). The infrared spectrum of this material showed CD stretching absorptions at 4.54, 4.63, and 4.77 μ and was otherwise similar to the nondeuterated sample.

The nmr spectrum of the deuterated **7**-d_2 showed a clean quartet centered at τ 4.15 and a doublet at 4.45 (2 H total). The large coupling of the quartet coincided with that of the doublet, *i.e.*, 10 cps. A broad absorption appeared at τ 7.3–7.9 (2 H) and other complex absorption appeared between 8.1 and 9 (4 H). The infrared spectrum showed CD stretching bands at 4.64, 4.71, and 4.82 μ. Other peaks appeared at 9.50, 10.05, 10.80, 11.33, 14.38, and 15.63 μ.

Mass Spectral Data.—The mass spectra of **5**-d_2, **6**-d_2, and **7**-d_2 were determined at 7 v on a CEC 21-103 C mass spectrometer. From a consideration of the relative intensities of the M, M − 1, and M − 2 peaks, the deuterium distributions of the three deuterated products, **5**-d_2, **6**-d_2, and **7**-d_2 could be calculated. Table II summarizes the data.[25]

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[18] D. Scharf and F. Korte, *Ber.*, **97**, 2425 (1964).

[19] It is believed that these product ratio differences are meaningful since considerable starting material was recovered.

[20] J. R. Edman, *J. Am. Chem. Soc.*, **88**, 3454 (1966), and E. Ciganek, *ibid.*, **88**, 2882 (1966), have provided examples of formally similar rearrangements in which aromatic rings assume the role of a double bond.

[21] H. E. Zimmerman, R. W. Binkley, R. S. Givens, and M. A. Sherwin, *ibid.*, **89**, 3932 (1967).

[22] J. Meinwald and G. W. Smith, *ibid.*, **89**, 4923 (1967); R. Srinivasan and K. H. Carlough, *ibid.*, **89**, 4933 (1967).

[23] C. Cupas, W. E. Watts, and P. von R. Schleyer, *ibid.*, **86**, 2503 (1964).

[24] Prepared by catalytic reduction of bicyclo[4.2.0]oct-7-ene: R. Srinivasan, *J. Am. Chem. Soc.*, **84**, 4141 (1962).

[25] Calculations were done by the method outlined by K. Bieman, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 228.

TABLE II
MASS SPECTRAL DATA

Compound	Observed intensities			Calcd % of deuterium		
	M	M − 1	M − 2	d_2	d_1	d_0
5	171.1	0.55	0.10			
5-d_2	186.3	22.1	3.4	87.9	10.4	1.6
6	288.0	0.95	0.30			
6-d_2	229.0	31.0	5.25	85.9	11.6	2.0
7	183.3	2.95	0.55			
7-d_2	189.1	24.5	4.35	86.8	11.2	2.0

Other Photolyses. Direct Irradiation.—A solution of 0.6 g of diene **5** in 20 ml of cyclohexane was irradiated in a quartz test tube for 11 days with the 2537-Å source in a Rayonet reactor.[26] In addition to starting material (~75%) and one new minor product, gas chromatographic analysis revealed the same two photoproducts **6** and **7** in the ratio of 1:4, respectively.

Mercury-Photosensitized Irradiation.—Diene **5** (2.0 g) and mercury (0.5 g) were placed in a 2 l. quartz flask along with enough glass wool to cover the liquids. The flask was flushed with dry nitrogen, cooled to −78°, and evacuated to 0.08 mm. The stopcock was closed and the flask was placed in the reaction chamber of the Rayonet reactor and exposed to 2537-Å light for 24 hr. The walls of the flask gradually became coated with polymer. At the end of the irradiation, 1.1 g of volatile material was removed from the flask by direct distillation under reduced pressure into a trap cooled in Dry Ice. Gas chromatographic analysis revealed the presence of **5**, **6**, and **7** in the ratios 14.3:1.45:1, respectively. The infrared spectra of the two products were superimposable with those obtained above.

Other Sensitizers.—Acetophenone, benzophenone, and fluorenone were investigated as sensitizers. Solutions of 0.25 g of **5** in 10 ml of cyclohexane and 0.05 g of ketone were irradiated in Pyrex with the 3500-Å source of the Rayonet reactor. Acetophenone was a reasonably good sensitizer in that after 24 hr there was formed a 17:4:1 mixture of **5**, **6**, and **7**. The other two ketones gave only traces of products after 80 hr of irradiation.

Registry No.—**5**, 4096-95-1; **5**-d_2, 15206-31-2; **6**, 3725-23-3; **6**-d_2, 15128-94-6; **7**, 15128-95-7; **7**-d_2, 15129-04-1.

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[26] S. N. E. Co., Middletown, Conn.

Addition of Organotin Hydrides to Internal Olefins[1a]

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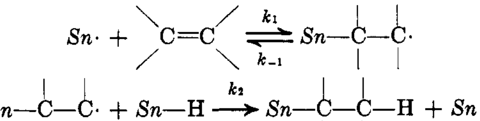
Contrary to earlier reports, it has been shown that organotin hydrides add to the double bonds of simple internal olefins and certain unreactive terminal olefins. The hydrostannations are possible by use of light for initiation, and very little side reaction is observed with trimethyltin hydride. Other catalysts, such as azobisisobutyronitrile, are relatively ineffective because the catalyst is consumed before significant hydrostannation of the olefin can occur. This is attributed to the high degree of reversibility of attack by organotin radicals on the double bonds involved. The following olefins have been shown to undergo photocatalyzed addition of trimethyltin hydride: 2-butene, 2-pentene, 2-methyl-2-butene, indene, cyclopentene, cyclohexene, cycloheptene, 1-methylcyclohexene, 1-cyano-3-cyclohexene, 1.4-cyclohexadiene, 2-ethyl-1-butene, 2.3-dimethyl-1-butene, and isobutylene.

Since the first report of the addition of organotin hydrides to olefins (hydrostannation),[2] a large number of olefins and acetylenes have been shown to undergo this reaction.[3] If the olefin is activated by the presence of groups such as phenyl, cyano, or carboalkoxy, the reaction occurs readily at moderate temperatures.[4] Less reactive olefins can be brought to reaction in the presence of free-radical sources such as azobisisobutyronitrile[5] or upon irradiation.[6,7] These facts, among others,[8] support the idea that the reaction of simple olefins occurs by a free-radical chain mechanism in which the propagation steps have been postulated to be eq 1 and 2.[3a,8]



$$Sn\cdot + \text{>C=C<} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Sn\text{—}\overset{|}{\underset{|}{\text{C}}}\text{—}\overset{|}{\underset{|}{\text{C}}}\cdot \qquad (1)$$

$$Sn\text{—}\overset{|}{\underset{|}{\text{C}}}\text{—}\overset{|}{\underset{|}{\text{C}}}\cdot + Sn\text{—H} \xrightarrow{k_2} Sn\text{—}\overset{|}{\underset{|}{\text{C}}}\text{—}\overset{|}{\underset{|}{\text{C}}}\text{—H} + Sn\cdot \qquad (2)$$

It has been reported that triethyltin hydride failed to add to cyclohexene or to methyl oleate in the presence of AlBN,[5] nor did dimethyltin dihydride add to 2-butene upon irradiation with ultraviolet light.[6b] Although the products of such additions should be thermodynamically stable, it was not apparent why the reactions appeared not to occur.

A probable explanation suggested itself when we observed that *cis*- and *trans*-2-butene were each isomerized to the same mixture of isomers when irradiated individually in the presence of trimethyltin hydride in the absence of solvent for 8 hr.[9] Furthermore, the reaction mixture contained a small amount of a new substance with the same retention time (glpc) as trimethyl-*sec*-butylin. Irradiation for 145 hr led to additional formation of this product which was isolated in 23% yield. Its identity was established

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