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.

Acknowledgments.—We are deeply indebted to the National Institutes of Health for financial support (RG 8701). The valuable assistance of Dr. Carl Schumway and Mr. E. Emery is also gratefully acknowledged.

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

Addition of Organotin Hydrides to Internal Olefins[1a]

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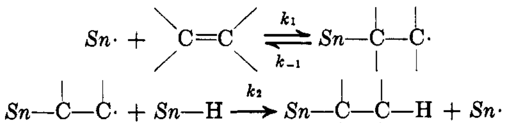
Contrary to earlier reports, it has been shown that organotin hydrides add to the double bonds of simple internal olefins and certain unreactive terminal olefins. The hydrostannations are possible by use of light for initiation, and very little side reaction is observed with trimethyltin hydride. Other 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]



$$Sn\cdot + \;{>}C{=}C{<}\; \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Sn-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\cdot \tag{1}$$

$$Sn-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\cdot + Sn-H \xrightarrow{k_2} Sn-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-H + Sn\cdot \tag{2}$$

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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[1] (a) This research was supported by the National Science Foundation under Grant GP-5285. (b) R. S. thanks the Deutschen Forschungsgemeinschaft for a travel grant. (c) To whom inquiries should be directed.

[2] G. J. M. van der Kerk, J. G. A. Luijten, and J. G. Noltes, *Chem. Ind.* (London), 352 (1956).

[3] For recent reviews, see (a) H. G. Kuivila, *Advan. Organometal. Chem.*, 1 47 (1964); (b) W. P. Neumann, *Angew. Chem.*, **76**, 849 (1964); (c) W. P. Neumann, Die Organische Chemie des Zinns, Enke Verlag, Stuttgart, 1967, p 67.

[4] J. G. Noltes and G. J. M. van der Kerk, "Functionally Substituted Organotin Compounds," Tin Research Institute, Greenford, England, 1958.

[5] W. P. Neumann, H. Niermann, and R. Sommer, *Ann.*, **659**, 27 (1962).

[6] (a) H. C. Clark, S. G. Furnival, and J. T. Kwon, *Can. J. Chem.*, **4**., 2889 (1963); (b) H. C. Clark and J. T. Kwon, *ibid*, **42**, 1288 (1964).

[7] J. Valade and J. C. Pommier, *Bull. Soc. Chim. France*, 199, 951 (1963).

[8] W. P. Neumann and R. Sommer, *Ann.*, **675**, 10 (1964).

[9] H. G. Kuivila and R. Sommer have shown that *cis*- and *trans*-2-butenes do not interconvert under the conditions of the experiment: *J. Am. Chem. Soc.*, **89**, 5616 (1967).

TABLE I

ADDITIONS OF TRIMETHYLTIN HYDRIDE TO INTERNAL DOUBLE BONDS AND DISUBSTITUTED TERMINAL OLEFINS

No.	Olefin	Product	Reaction time, hr	Yield, %	Bp, °C (mm)	$n^{20}D$	Formula	Calcd, %			Found, %		
								C	H	Sn	C	H	Sn
1	2-Butene	**1**	145	23	146–148 (760)	1.4630	$C_7H_{18}Sn$	38.06	8.21	53.73	38.29	8.28	...
2	2-Pentene	**2 and 3**	340	33	69 (25)	(1.4669)	$C_8H_{20}Sn$	40.90	8.58	50.52	40.70	8.70	51.4
3	2-Methyl-2-butene	**4**	270	51	71–72 (30)	1.4669	$C_8H_{20}Sn$	40.90	8.58	50.52	40.69	8.57	50.4
4	Indene	**5**	235	98	128 (10)	1.5508	$C_{12}H_{18}Sn$	51.30	6.46	42.24	51.50	6.45	41.9
5	Cyclopentene	**7**	140	76	77 (25)	1.4884	$C_8H_{18}Sn$	41.25	7.79	50.96	41.09	7.78	51.3
6	Cyclohexene	**8**	240	49	74–76 (10)	1.4937	$C_9H_{20}Sn$	43.77	8.16	48.06	43.59	8.24	47.6
7	Cycloheptene	**9**	270	26	95–96 (10)	1.5018	$C_{10}H_{22}Sn$	46.02	8.50	45.48	46.29	8.60	45.6
8	1-Methylcyclohexene	**10**	235	61	88–89 (10)	1.5003	$C_{10}H_{22}Sn$	46.02	8.50	45.48	46.19	8.25	45.6
9	1-Cyano-3-cyclohexene	**12 and 13**	260	52	138–140 (13)	(1.5061)	$C_{10}H_{19}NSn$	44.16	7.04	43.64	44.45	6.92	43.5
10	1.4-Cyclohexadiene	**14**	250	37	80–82 (12)	1.5067	$C_9H_{18}Sn$	44.14	7.41	48.46	44.21	7.57	48.6
11	2-Ethyl-1-butene	**15**	240	97	182–184 (760)	1.4654	$C_9H_{22}Sn$	43.42	8.91	47.67	43.47	8.77	47.5
12	2.3-Dimethyl-1-butene	**16**	80	98	80 (22)	1.4649	$C_9H_{22}Sn$	43.42	8.91	47.67	43.54	9.07	47.7
13	Isobutylene	**17**	90	96	58 (37)	1.4552	$C_7H_{18}Sn$	38.06	8.21	53.73	38.21	8.20	53.4

by comparison of its nmr and infrared spectra with those of authentic trimethyl-*sec*-butylin. Only negligible amounts of decomposition products such as tetramethyltin, hexamethylditin, and metallic tin were formed and most of the unreacted trimethyltin hydride was recovered. These observations indicate that the attack by trimethyltin radicals on 2-butene is highly reversible; *i.e.*, $k_{-1} > k_2[SnH]$ and only a very small fraction of events occurring in step 1 forward are consummated by product formation in step 2.

The absence of reaction in the cases cited above can be attributed to the competition between olefin and the N=N bond for the organotin hydride as it is known that organotin hydrides add to azo compounds, too.[3b] Yet, recently it was found that even by AlBN catalysis addition of trialkyltin hydrides to cyclohexene and cyclopentene occurs to a certain extent.[10] The lack of addition of dimethyltin dihydride to 2-butene[6] is probably due to the fact that the decomposition of the dimethylhydridotin radicals occurs much more rapidly than step 2.

Presumably the kinetic balance between decomposition of trimethyltin radicals and the occurrence of step 2 with 2-butene is favorable. Therefore, it appeared to be worthwhile to study the photocatalyzed addition of trimethyltin hydride to other "unreactive" olefins. Thirteen olefins were included in the survey with the results summarized in Table I. In each case, except that of indene, trimethyltin hydride was still present when the reaction mixture was worked up. Thus, the yields reported are not necessarily the highest attainable.

Structures of products are shown in Chart I. Although a cyano group in an olefin does not interfere with the addition reaction, as shown in the case of 4-cyanocyclohexene, the carbonyl group of 4-formylcyclohexene reacts more readily with the tin hydride than the C=C bond, as should be expected,[11] leading to 1-trimethylstannoxymethylcyclohexene-3 when the reactants were used in equimolar amounts.

Additions of organotin hydrides to olefins of the type $H_2C{=}CRR'$ (both R and R′ are simple alkyl groups) do not occur without a catalyst and are not very satisfactory even with AIBN catalysis.[12] With ultraviolet irradiation, these additions proceed smoothly and in excellent yields. Three examples are included in Table I (entries 11, 12, and 13).

The structures of the addition products to 2-butene, cyclopentene, cyclohexene, cycloheptene, and 1.4-cyclohexadiene are unambiguous. Attack of the trimethyltin radical on either C-2 or C-3 of 2-pentene results in the formation of a secondary carbon radical and, therefore, little or no preference should be expected. The addition product contained two isomers (**2** and **3**) in the ratio 55:45. With 2-methyl-2-butene, the attack of the trimethyltin radical could lead to either a secondary or a tertiary carbon radical, the latter being the expected one. It would give rise to trimethyl(3-methyl-but-2-yl)tin (**4**). The nmr spectrum was in much better agreement with that expected for this compound than of trimethyl-*t*-amyltin. An authentic sample of trimethyl-*t*-amyltin showed a retention time (glpc) different from that of the addition product.

Tetramethylethylene, which, on attack by an organotin radical, also would give rise to a tertiary radical, failed to react to a significant extent upon irradiation for 200 hr.

The nmr spectrum of the hydrostannation product of indene showed an A_2B_2X pattern[13] which would be expected for trimethylindan-2-yltin (**5**); a and b appeared as a four-proton multiplet at τ 7.05, c as a one-proton quintet at 8.32. Structure **5** is in agreement with expectation, as the attack of the tin radical in the 2 position gives rise to a stabilized benzyl radical. The presence of a small amount of **6** could not be excluded by the nmr spectrum. Since **6** is a benzyltin, it should be cleaved by iodine at room temperature.[14] The addition product did not discolor an iodine solution, thus making contamination with **6** unlikely. In other free-radical additions to indene only the products analogous to **5** are formed.[15] For the same reasons as discussed above for the additions to 2-methyl-2-butene, the hydrostannation of 1-methylcyclohexene should yield **10** rather than **11**. In the nmr spectrum of the adduct, the methyl protons appear as a three-proton doublet (τ 8.14, J = 12 cps) consistent with **10**, whereas the methyl protons of **11**

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[10] W. P. Neumann, private communication.

[11] J. C. Pommier and J. Valade, *Bull. Soc. Chim. France*, 975 (1965).

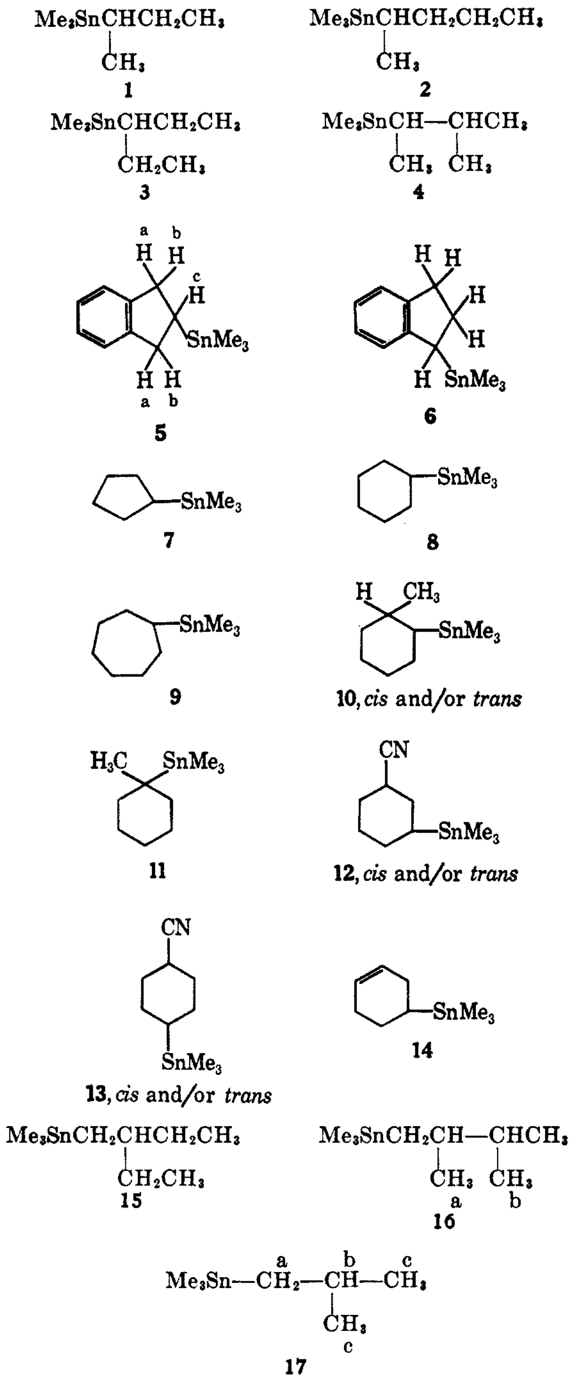
[12] R. Sommer, Ph.D. Thesis, Giessen, 1964.

[13] "Nuclear Magnetic Resonance for Organic Chemists," D. W. Mathieson, Ed., Academic Press Inc., New York, N. Y., 1967.

[14] See ref 3c, p 29.

[15] M. S. Kharasch and H. N. Friedlander, *J. Org. Chem.*, **14**, 239 (1949); P. D. Readio and P. S. Skell, *ibid.*, **31**, 759 (1966); A. A. Oswald, K. Griesbaum, and W. Naegle, *J. Am. Chem. Soc.*, **86**, 3791 (1964).

Chart I



should appear as a singlet. (The protons of the trimethyltin group appeared at τ 9.82.) From the nmr spectrum it could not be determined whether **10** is the *cis* or the *trans* isomer or a mixture of both. Yet glpc, run under conditions where a separation of the 4-cyanocyclohexene adducts could be obtained, showed only one peak. In the addition to 4-cyanocyclohexene three of the possible four isomers of **12** and **13** could be detected. One of these isomers predominated. The stereochemistry of these additions remains to be investigated.

In the hydrostannations of terminal olefins, one would conclude by analogy with other free-radical hydrostannations[16,17] that the tin would become attached to the terminal carbon. This would be even more favorable in the cases of the disubstituted terminal olefins, since the more easily formed intermediate would be a tertiary rather than a secondary carbon radical (as in the case of organotin radical attack on the terminal position of $H_2C{=}CHR$). The nmr spectrum of the isobutylene adduct showed a two-proton doublet at τ 9.13 (J = 6 cps) for a, a six-proton doublet at 9.05 (J = 6 cps) for c, and a one-proton multiplet at 8.07 for b. (The protons of the trimethyltin group appeared at τ 9.95.) Therefore, trimethylisobutyltin (**17**) was formed rather than trimethyl-*t*-butyltin.

The product of addition to 2,3-dimethyl-1-butene was **16**, trimethyl(2,3-dimethylbut-1-yl)tin, since the nmr spectrum consisted of a nine-proton doublet (for a and b) at τ 9.18, J = 7 cps. (The other possible isomer, trimethyl(2,3-dimethyl-but-2-yl)tin, should show two six-proton doublets.) The structure of the hydrostannation product of 2-ethyl-1-butene as **15** is assigned only by analogy, since the nmr spectrum was too complex for first-order interpretation.

Other trialkyltin hydrides like trimethyl- and tributyltin hydride can, in principle, also be added to internal olefins. When we irradiated these tin hydrides with 2-methyl-2-butene or cyclohexene, analysis by glpc indicated that some addition did occur. However, the reaction mixtures very soon became yellow on irradiation and the yields of adducts were too small for characterization.

Organotin hydrides have an absorption maximum below 190 mμ. Therefore, it seemed puzzling that the reactions could be initiated by irradiation through Pyrex which has a cut-off at about 280 mμ, but in the concentration range used in the hydrostannations, there is still some absorption ($\epsilon \simeq 0.25$) even at 390 mμ. When we irradiated a mixture of trimethyltin hydride and cyclohexene in a Pyrex or a quartz vessel under similar conditions for 24 hr, the reaction mixture in the Pyrex tube contained about two to three times as much addition product as the one in the quartz tube. In the quartz tube much of tin hydride was decomposed to metallic tin, whereas in the Pyrex tube no significant decomposition had occurred.

Experimental Section

Boiling points are uncorrected. Carbon-hydrogen analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Tin analyses were carried out by oxidation to stannic oxide with a 1:1 (volumes) mixture of concentrated sulfuric and nitric acid in quartz test tubes as described.[18] The nmr spectra were recorded on a Varian A-60A instrument in CCl_4 solutions, using tetramethylsilane as an internal standard after integration. For glpc separations, an F & M Model 720 temperature-programmed gas chromatograph was used with a flow rate of 60 ml/min of helium, using a 20-ft column, silicone rubber SE 30, 10% on Chromosorb W 60-80. Before distillation all reaction mixtures were checked on this column, 40-290°, 10 or 15°/min.

Materials.—All olefins were obtained from commercial sources. 4-Cyanocyclohexene and cyclohexene-4-carboxaldehyde were gifts from the Dow Chemical Co. 2-Butene and 2-methylpropene were used directly from cylinders; the other olefins were redistilled before use. Cyclohexene, stabilized with hydroquinone, was purified by shaking with a 2 *N* sodium hydroxide solution and then with water to remove the stabilizer. 1,4-Cyclohexadiene, stabilized with hydroquinone, was used without removing the stabilizer.

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[16] W. P. Neumann, unpublished results (mentioned in ref 3c, p 68).

[17] A. J. Leusink and J. G. Noltes, *Tetrahedron Letters*, 335 (1966).

[18] W. P. Neumann, *Ann.*, **653**, 157 (1962).

Trimethyltin hydride was prepared by a method suggested by Neumann,[19] using tributyltin hydride as reducing agent for trimethyltin chloride. A two-necked flask equipped with a three-way stopcock was connected to a Claisen head and a trap. The flask was filled under exclusion of air with 160 g (0.55 mole) of tributyltin hydride. Under magnetic stirring 100 g (0.5 mole) of trimethyltin chloride was dissolved in the tributyltin hydride. The trimethyltin hydride was distilled at 10–15 mm into the trap, cooled with liquid nitrogen. During the distillation, the flask was heated slowly to 50° and maintained at this temperature for 1 hr. The trimethyltin hydride was redistilled, bp 60° (760 mm). Yields between 90 and 95% were obtained. (The tributyltin chloride can be reconverted into tributyltin hydride.)

Hydrostannations. Typical Procedure.—An ampoule of Pyrex glass was evacuated, heated, and filled with argon. Trimethyltin hydride (4.94 g, 0.03 mole) and 2-methyl-2-butene (3.51 g, 0.05 mole) were placed in the ampoule under a stream of argon and sealed after cooling to −78°. The ampoule was then irradiated with a 100-w medium-pressure mercury vapor lamp at 10-15°. After irradiation, the excess of 2-methyl-2-butene and the unreacted trimethyltin hydride were recovered by distillation at 760 mm. The addition product was obtained in 3.55-g (51%) yield, bp 71–72° (30 mm). Traces of hexamethylditin were converted into the hydroxide which was filtered off. The product was examined by glpc, 125°, isothermal.

In the experiments with 2-butene and 2-methylpropane, the olefins were condensed from the tank into the air-free ampoules at −78° and the trimethyltin hydride was added. In the experiments with less volatile olefins, the irradiations were carried out in two-necked ampoules equipped with a three-way stopcock, rather than in sealed ampoules.

1-Trimethylstannoxymethyl-3-cyclohexene.—Freshly distilled 3-cyclohexene-1-carboxyaldehyde (3.3 g, 0.03 mole) and 4.94 g (0.03 mole) of trimethyltin hydride were sealed under exclusion of air in a Pyrex ampoule and irradiated as described above. After 190 hr, the reaction mixture was checked by infrared spectroscopy; the Sn—H and C=O absorption had disappeared, whereas the C=O bond was still present. Distillation gave 6.0 g (73%) of the addition product, bp 104–106° (760 mm).

Anal. Calcd for $C_{10}H_{20}OSn$: Sn, 43.17. Found: Sn, 42.6.

Trimethyl-*t*-amyltin.—A Grignard reagent was prepared from 42.6 g (0.4 mole) of *t*-amylchloride and 14.6 g (0.6 mole) of magnesium in 400 ml of ether and reacted with 39.9 g (0.2 mole) of trimethyltin chloride. After refluxing for 1 hr, the mixture was hydrolyzed, the organic layer separated and dried over magnesium sulfate, the ether distilled off, and 27.1 g of product collected by distillation on a 20-cm column, packed with glass helices, bp 156–158° (760 mm). It was contaminated by small amounts of two other compounds. The product was purified by glpc (35-ft silicone rubber, 10% on Chromosorb W, 130° isothermal), mp 46–48°.

Anal. Calcd for $C_8H_{20}Sn$: C, 40.90; H, 8.58. Found: C, 40.95; H, 8.56.

Registry No.—**1,** 15095-79-1; **2,** 15095-80-4; **3,** 15095-81-5; **4,** 15095-82-6; **5,** 15095-83-7; **7,** 15095-84-8; **8,** 3531-48-4; **9,** 15095-93-9; **10** (*cis*), 15095-94-0; **10** (*trans*), 15095-85-9; **13** (*cis*), 15095-95-1; **13** (*trans*), 15095-86-0; **14,** 15095-87-1; **15,** 15095-88-2; **16,** 15095-89-3; **17,** 1118-10-1; trimethyltin hydride, 1631-73-8; 1-trimethylstannoxymethyl-3-cyclohexene, 15095-91-7; trimethyl-*t*-amyltin, 15095-92-8.

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(19) W. P. Neumann and J. Pedain, *Tetrahedron Letters*, 2461 (1964).

Photoalkylation of Cyclic Acetals

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The acetone-, acetophenone-, and benzophenone-initiated photochemical addition of olefins to 1,3-dioxolan and 1,3,5-trioxan is described. The addition of terminal olefins to 1,3-dioxolan leads to 2-alkyl-1,3-dioxolans (1:1 adducts) as the major products in yields of up to 50%; with diethyl maleate, diethyl (1,3-dioxolanyl-2)-succinate may be obtained in yields of up to 90%. The corresponding reaction with 1,3,5-trioxan leads to 2-alkyl-1,3,5-trioxans in yields of up to 25% with terminal olefins and 84% with diethyl maleate.

The photoalkylation of cyclic ethers with olefins has been described by us recently.[2] This reaction leads to the formation of α-alkylated ethers resulting from substitution of an α hydrogen in the cyclic ether molecule by an alkyl group. The alkylation of cyclic acetals by a similar procedure would provide a new method for the synthesis of valuable organic intermediates, such as monoalkylated 1,3-dioxolans and 1,3,5-trioxans. This work was undertaken in an attempt to develop this method as a simple and general procedure for the alkylation of various acetals. Since mild acid treatment of acetals leads to the corresponding aldehydes, this alkylation reaction of acetals would constitute a new route for the synthesis of aldehydes from olefins. Further, 1,3,5-trioxan is a known monomer for a variety of polymers[3] and the previously unknown monoalkyl 1,3,5-trioxans would be potential monomers for polymerization and the present procedure of photoalkylation serves as a method for their preparation using 1,3,5-trioxan as a starting material. It is worth noting that some of the photochemical reactions of acetals may also be useful for studying photochemical transformation of sugars.[4]

Results

The light-induced addition of cyclic acetals to terminal olefins has been reported by us recently in a preliminary communication.[5] We have since extended this reaction to a variety of olefinic systems and the present paper includes full details of the reactions and the products isolated.

1,3-Dioxolan and 1,3,5-trioxan were found to undergo an acetone-, acetophenone-, and benzophenone-initiated photochemical addition to terminal olefins and diethyl maleate to give the 1:1 adducts as the major products of the reaction. The reactions

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(1) In partial fulfillment of the requirements for a Ph.D. degree submitted to the Feinberg Graduate School of The Weizmann Institute of Science.

(2) I. Rosenthal and D. Elad, *Tetrahedron*, **23**, 3193 (1967).

(3) W. Kern, H. Deibig, A. Giefer, and J. J. Jaacs, *Pure Appl. Chem.*, **12**, 371 (1966); S. Okamura, K. Hayashi, and Y. Kitanishi, *J. Polymer Sci.*, **58**, 925 (1962), and references cited therein.

(4) For a review, see G. O. Phillips, *Advan. Carbohydrate Chem.*, **18**, 9 (1963).

(5) D. Elad and I. Rosenthal, *Chem. Commun.*, No. 19, 684 (1966).