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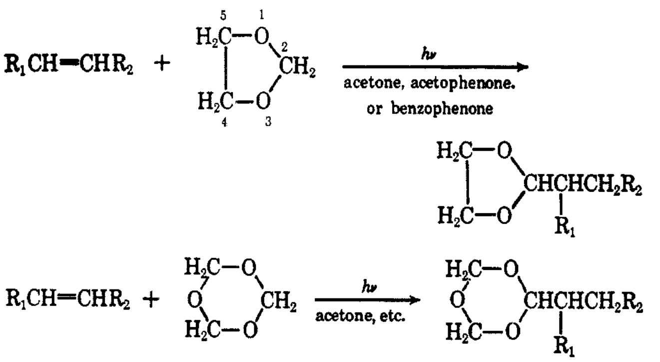
[1] In partial fulfillment of the requirements for a Ph.D. degree submitted to the Feinberg Graduate School of The Weizmann Institute of Science.

[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).



a, R_1 = H; R_2 = C_5H_{11}, C_6H_{13}, C_8H_{17}, $C_{10}H_{21}$, $H_3CCOO(CH_2)_2$, $H_3CCOO(CH_2)_8$,
b, $R_1 = R_2 = COOC_2H_5$

studied and the major products obtained are summarized in Tables I and II.

TABLE I
ADDITION PRODUCTS OF 1,3-DIOXOLAN AND OLEFINS[a]
(INITIATED BY ACETONE)

Olefin	1:1 addition products,[b] %
1-Heptene	2-Heptyl-1,3-dioxolan, 28,[c] 35[d] 4-Heptyl-1,3-dioxolan, 5[c]
1-Octene	2-Octyl-1,3-dioxolan, 25[c] 4-Octyl-1,3-dioxolan, 2[c]
1-Decene	2-Decyl-1,3-dioxolan, 33,[c] 50[d] 4-Decyl-1,3-dioxolan, 3,[c] 3[d]
1-Dodecene	2-Dodecyl-1,3-dioxolan, 35[c] 4-Dodecyl-1,3-dioxolan, 6[c]
Methyl 4-pentenoate	Methyl 5-(1,3-dioxolanyl-2)-pentanoate, 18[c] Methyl 5-(1,3-dioxolanyl-4)-pentanoate, 2[c]
Methyl 10-undecylenate	Methyl 11-(1,3-dioxolanyl-2)-undecanoate, 19[c]
Diethyl maleate	Diethyl (1,3-dioxolanyl-2)-succinate, 90[e]

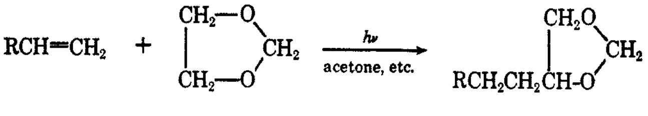
[a] The mole ratio of 1,3-dioxolan–olefin was 20:1 for terminal olefins and 70:1 for diethyl maleate. [b] Yields are based on the olefins employed. The consumptions were nearly quantitative in most cases. The ratio between isomers was determined by the intensity of corresponding peaks in glpc. [c] Hanau Q81 high-pressure mercury vapor lamps fitted into Pyrex tubes were used as the radiation source for these reactions. [d] In sunlight. [e] Initiated by acetophenone.

TABLE II
ADDITION PRODUCTS OF 1,3,5-TRIOXAN AND OLEFINS[a]
(INITIATED BY ACETONE)

Olefin	1:1 addition product,[b] %
1-Heptene	Heptyl-1,3,5-trioxan, 15[c]
1-Octene	Octyl-1,3,5-trioxan, 20,[c] 19[d]
1-Decene	Decyl-1,3,5-trioxan, 21,[c] 21,[d] 20[e]
1-Dodecene	Dodecyl-1,3,5-trioxan, 24[c]
Methyl 4-pentenoate	Methyl 5-(1,3,5-trioxanyl)-pentanoate, 10[c]
Methyl 10-undecylenate	Methyl 11-(1,3,5-trioxanyl)-undecanoate, 19,[c] 15[d]
Diethyl maleate	Diethyl (1,3,5-trioxanyl)-succinate, 27,[c] 84[e]

[a] The mole ratio of 1,3,5-trioxan–olefin was 20:1 for terminal olefins and 70:1 for diethyl maleate. [b] Yields are based on the olefins employed. The consumptions were nearly quantitative in most cases. [c] Hanovia 450-w high-pressure mercury vapor lamps fitted into Pyrex tubes were used as the radiation source for these reactions. Temperature of reaction *ca.* 65°. [d] In sunlight. [e] Initiated by acetophenone.

1,3-Dioxolan gave both types of 1:1 adduct. The 2-alkyl derivatives were characterized by their physical properties and were compared with authentic samples prepared by treating the appropriate aldehyde with ethylene glycol. They were further hydrolyzed by dilute mineral acids to the corresponding aldehydes which were compared with authentic samples. The 4-alkylated derivatives resulting from substitution of a hydrogen atom at C_4 in the 1,3-dioxolan molecule by an alkyl group could also be isolated, though in poorer yields. Their formation can be formulated as

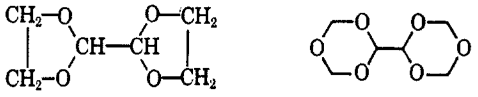


These products were characterized by comparison with authentic samples and further by hydrolysis with dilute mineral acids to the appropriate diols.

The monoalkylated 1,3,5-trioxans were characterized through elemental analyses, spectroscopic data, and hydrolysis to formaldehyde and the appropriated aldehydes which were compared with authentic samples.

Addition products of the photoinitiator moiety and the olefins, such as 2-methyl-2-alkanols and alkyl methyl ketones, were also obtained and identified by standard procedures as described in previous publications.[2,6] Increasing the amount of acetone (to increase the solubility of 1,3,5-trioxan) resulted in larger quantities of addition products of the acetone moiety to the olefins.

Dehydro dimers of the structures shown below



were formed in all reactions of 1,3-dioxolan and 1,3,5-trioxan, respectively. They were characterized by elemental analyses, spectroscopic data, and acid hydrolysis to glyoxal.

Some difficulties were encountered in attempting to dissolve 1,3,5-trioxan in the reaction mixture. These were overcome by raising the temperature of the reaction to 65° when more 1,3,5-trioxan could be dissolved and higher 1,3,5-trioxan–olefin ratios could be employed. Improved yields of the 1:1 addition products with olefins were obtained at this temperature.

Discussion

The various aspects of the direct light-induced and the ketone-initiated photochemical addition reactions of a variety of hydrogen donors (*e.g.*, formamide and cyclic ethers) have been discussed in previous publications of this series.[2,6] The light-induced addition of acetals to olefins resembles in some respects the corresponding reactions of ethers and olefins. The transition of lowest energy in acetals is of the n → σ* type and involves absorption of light shorter than

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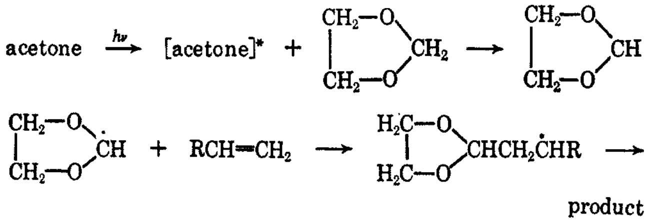
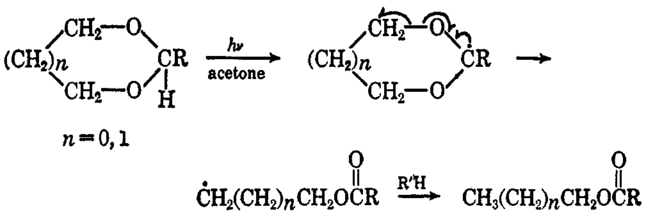
(6) D. Elad and J. Rokach, *J. Org. Chem.*, **29**, 1855 (1964); **30**, 3361 (1965).

2000 Å.[7] Thus, direct excitation of acetals should require ultraviolet light of short wavelengths.[8] The present ketone-initiated photochemical reactions of acetals and olefins are induced by light of wavelengths longer than 2900 Å and involve absorption of light by the ketonic compound through its n → π* transition. It seems to us that the next step involves an abstraction of a hydrogen atom from the acetal molecule by the photoactivated carbonyl compound. This assumption is supported by the formation of isopropanol and 2-methyl-2-alkanols and benzpinacol when acetone or benzophenone were used as initiators, respectively. These products indicate a hydrogen atom abstraction step from the acetal by the photoactivated ketone molecule.[9]

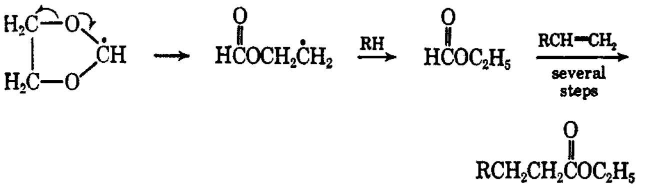
The acetal free radical obtained is subsequently trapped by the olefin, leading to the substituted acetal. Hence the reaction of 1,3-dioxolan and olefins can be formulated as



Acetal free radials do not seem to be very stable[10] and tend to lose an alkyl radical even at room temperature.[11] Cyclic acetal free radicals undergo ring decyclization by a similar process. Although a few cases are known where these radicals have been trapped unchanged,[12] attempts to react acetals through free-radical intermediates lead usually to derivatives of the corresponding carboxylic esters.[13] Thus, irradiation of cyclic acetals of aldehydes in the presence of acetone leads to the appropriate carboxylic esters by the route[14]

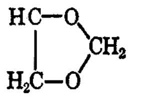


This fact makes the preservation of the acetal group or ring in cyclic acetals in free-radical reactions more difficult than with the corresponding ether analogs. Experimental results show that terminal olefins and diethyl maleate serve as good scavengers for the cyclic acetal radicals which are trapped before undergoing decyclization. However, some decyclization of the acetal ring takes place under the reaction conditions as evidenced by the formation of ethyl formate and ethyl esters of higher carboxylic acids produced according to the mechanism

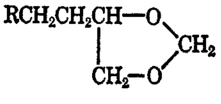


Another possibility for the formation of the ethyl esters of the higher carboxylic acids is through hydrogen atom abstraction from the 2-alkyl-1,3-dioxolan.[15]

The acetal CH bond ($-OCH_2O-$) has enhanced reactivity owing to its activation by two adjacent oxygen atoms.[16] This hydrogen is in fact abstracted by the photoactivated carbonyl compound to produce the acetal radical,[17] which is stabilized by electron delocalization involving two oxygen atoms. However, the ether $-CH$ bonds (C_4 and C_5 in dioxolan) in the same molecule are also activated and can also be abstracted to yield the corresponding ether radical following.



These radicals subsequently add to the olefinic substrate leading to 4-alkyl-1,3-dioxolans shown below.



Hydrolysis of these compounds by dilute mineral acids led to the corresponding diols $RCH_2CH_2C(OH)HCH_2OH$. However, the 4-alkylated acetals were minor products of the reactions.

As in the case of cyclic ethers and other addends,[2,6] the addition of cyclic acetals to diethyl maleate proceeded smoothly, leading to high yields of the 1:1 adducts when using acetophenone as photoinitiator.

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(7) G. J. Hernandez and A. B. F. Duncan, *J. Chem. Phys.*, **36**, 1504 (1962); B. C. Roquitte, *J. Phys. Chem.*, **70**, 2863 (1966); H. Nauta in "Reactivity of Solids," G. M. Schwab, Ed., Elsevier Publishing Co., 1965, p 162.

(8) The reactions of 1,3-dioxolan and terminal olefins could be induced by the unfiltered (quartz sleeve) light of the radiation source leading to poor yields of the 1:1 addition products. In the corresponding reactions of 1,3,5-trioxan no 1:1 addition product could be detected. It should be stressed that impurities, such as aldehydes, present in trace amounts in the 1,3-dioxolan, may initiate the addition reaction through light absorption and, therefore, the direct light-induced reaction does not necessarily involve an excited 1,3-dioxolan molecule.

(9) The possibility of energy transfer from the excited ketone to the acetal seems less probable since the triplet energies of acetals, though yet unknown, are probably high in comparison with those of the ketones employed. However, such a possibility should not be ignored.

(10) L. P. Kuhn and C. Wellman, *J. Org. Chem.*, **22**, 774 (1957); E. S. Huyser, *ibid.*, **25**, 1820 (1960); C. L. Aldrige, J. B. Zachry, and E. A. Hunter, *ibid.*, **27**, 47 (1962); E. S. Huyser and Z. Garcia, *ibid.*, **27**, 2716 (1962); E. S. Huyser, R. M. Kellog, and D. T. Wang, *ibid.*, **30**, 4377 (1965); E. S. Huyser and D. T. Wang, *ibid.*, **29**, 2720 (1964).

(11) *Cf.* E. N. Marwell and M. J. Joncich, *J. Am. Chem. Soc.*, **73**, 973 (1951); J. B. Wright, *ibid.*, **77**, 4883 (1955); I. Tanasescu and S. Mager, *Acad. Rep. Populare Romine, Filiala Cluj, Studii Cercetari Chem.*, **13** (1), 69 (1962); *Chem. Abstr.*, **59**, 11637 (1963), and similar reactions in this series; J. D. Prugh and W. C. McCarthy, *Tetrahedron Letters*, 1351 (1966); J. E. Baldwin and E. Walker, *J. Am. Chem. Soc.*, **88**, 4191 (1966).

(12) T. M. Patrick Jr., U. S. Patent 2,716,660 (1955); U. S. Patent 2,628,238 (1953); U. S. Patent 2,684,373 (1954). A. Nagasaka, R. Oda, and S. Nukina, *Kogyo Kagaku Zasshi*, **57**, 169 (1954); *ibid.*, **58**, 46 (1955). A. Nagasaka, S. Nakamura, and R. Oda, *ibid.*, **58**, 460 (1955). R. C. Cookson, I. D. R. Stevens, and C. T. Watts, *Chem. Commun.*, No. 12, 259 (1965). These references report cases confined to "activated" double bonds, such as maleates.

(13) We have found recently that alkylation of 1,3,5-trioxan with terminal olefins using peroxides as initiators can be induced at elevated temperatures without undergoing ring decyclization: I. Rosenthal and D. Elad, submitted for publication.

(14) D. Elad and R. D. Youssefyeh, *Tetrahedron Letters*, 2189 (1963).

(15) *Cf.* T. J. Wallace and R. J. Gritter, *J. Org. Chem.*, **27**, 3067 (1962).

(16) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc. New York, N. Y. 1957, p 287; G. Sosnovsky, "Free Radical Reactions in Preparative Organic Chemistry," The Macmillan Co., New York, N. Y., 1964, p 140.

(17) N. Nozaki, S. Fujita, H. Takaya, and R. Noyari, *Tetrahedron*, **23**, 45 (1967).

The use of acetone as a photoinitiator led to poorer yields in the case of 1,3,5-trioxan.

The photoaddition of hydrogen donors to α,β-unsaturated esters and the problems involved, such as energy transfer from the excited ketone to the α,β-unsaturated ester and its competitive effect on the hydrogen atom abstraction process, have already been discussed in our previous publications.[2,18]

The products of the reactions of cyclic acetals and olefins, *i.e.*, 1:1 anti-Markovnikov adducts, telomers, and dehydro dimers, as well as products derived from the photoinitiator moiety, are in accord with what might be expected as a free-radical chain process. A similar mechanism has already been suggested by us for a previous photoreaction of this type.[6]

Experimental Section[19]

Experiments with ultraviolet light were conducted in an immersion apparatus using Hanau Q 81 and Hanovia 450S high-pressure mercury vapor lamps for the 1,3-dioxolan and 1,3,5-trioxan experiments, respectively. The lamps were cooled internally by running water. Typical experiments are described under A. Other experiments were carried out under similar conditions. Pyrex filters were employed unless otherwise stated.

Unidentified oils were isolated in several cases in the course of the chromatographic separations (for details and proposed partial structures, see I. Rosenthal, Ph.D. Dissertation, The Weizmann Institute of Science, Rehovoth, 1967).

Reagents.—1,3-Dioxolan was freshly distilled over sodium and checked for carbonyl absorption before use. 1,3,5-Trioxan (Aldrich) was used with no purification. The authentic 2-alkyl-1,3-dioxolans were prepared from the appropriated aldehydes and ethylene glycol by standard procedures. The 4-alkyl isomers were prepared from the corresponding diols and formaldehyde.

A. 1,3-Dioxolan, 1-Decene, and Acetone. 1. With Ultraviolet Light.—A mixture of 1,3-dioxolan (110 ml), acetone (8 ml), and 1-decene (1.01 g) was irradiated for 1 hr. A solution of 1-decene (10 g) in acetone (8 ml) was then added in eight equal portions at 1-hr intervals and the mixture was further irradiated until consumption of the olefin was complete (*ca.* 72 hr). Excess reagents were removed under reduced pressure and the distillate was shown to contain 1,3-dioxolan, acetone, isopropyl alcohol, and ethyl formate (glpc; Carbowax 400 at 100°). The residue (17 g), whose infrared spectrum showed only weak carbonyl absorption, was chromatographed on alumina. Elution with petroleum ether (bp 60–80°) gave 2-tridecanone (0.2 g) followed by 2-decyl-1,3-dioxolan (5.52 g, 32.8%): bp 172–174° (35 mm); $n^{25}\mathrm{D}$ 1.4389; nmr, multiplets at 5.18 (1 H, $-OCHO-$) and 6.14 (4 H, $-OCH_2CH_2O-$), a broad signal at 8.7 (18 H, $-(CH_2)_9CH_3$), and a triplet at 9.1 (3 H, $-CH_2CH_3$).

Anal. Calcd for $C_{13}H_{26}O_2$; C, 72.84; H, 12.23. Found: C, 72.61; H, 12.06.

Hydrolysis of the product (1 g) was achieved by heating under reflux for 1 hr, with 5% sulfuric acid (using dioxane as an homogenizer), giving undecanal in 92% yield. The 2,4-dinitrophenylhydrazone showed mp 100–101° (lit.[20] mp 104°). The same solvent further eluted 4-decyl-1,3-dioxolan (0.6 g, 3.5%): bp 110–112° (2 mm); $n^{20}\mathrm{D}$ 1.4403; nmr, two sharp signals at 5.04 and 5.2 (2 H, $-OCH_2O-$), a multiplet at 6.18 (2 H, $-OCHCH_2O-$) and apparent triplet at 6.62 (1 H, $C_{10}H_{21}$-$CHO-$), a broad signal at 8.7 (18 H, $-(CH_2)_9CH_3$), and a triplet at 9.1 (3 H, $-CH_2CH_3$).

Anal. Calcd for $C_{13}H_{26}O_2$: C, 72.84; H, 12.23. Found: C, 73.38; H, 12.31.

Acid treatment of the product led to 1,2-dodecanediol, mp 58–59° (lit.[21] mp 60–61°). (An authentic sample was prepared by the method of Swern, *et al.*[21]). Petroleum ether–ether (9:1) eluted ethyl undecanoate (0.1 g). The same solvent mixture (2:3) eluted 2-methyl-2-dodecanol (2.58 g) and 2,2′-bi-1,3-dioxolan (0.3 g) (with 1:4 mixture): mp 110–111° (petroleum ether) (lit.[22] mp 109–112°); nmr, a singlet at 5.1 (2 H, $-CHCH-$) and a multiplet at 6 (8 H, $-OCH_2CH_2O$). Treatment of the product with 2,4-dinitrophenylhydrazine reagent led to glyoxal 2,4-dinitrophenylhydrazone, mp *ca.* 310° dec (lit.[23] mp 318° dec). Ether–alcohol mixtures eluted polar oils (3.2 g).

Anal. Found: C, 70.20; H, 11.98.

2. In Sunlight.—A mixture of 1,3-dioxolan (110 ml), acetone (8 ml), and 1-decene (2 g) was left in direct sunlight for 1 day. A solution of 1-decene (9.01 g) in acetone (8 ml) was then added in seven equal portions at 1-day intervals and the mixture was left in sunlight for another 8 days. Excess reagents were removed under reduced pressure and the residue (20 g) was chromatographed on alumina. Petroleum ether eluted an oil (1 g) believed to be a mixture of telomers followed by 2-decyl-1,3-dioxolan (8.5 g, 50%), 4-decyl-1,3-dioxolan (0.5 g, 3%), and 2-dodecanone (0.2 g, identified by glpc). Petroleum ether–ether eluted 2-methyl-2-dodecanol (2.9 g) followed by 2,2′-bi-1,3-dioxolan (0.3 g) and polar oils (3.9 g).

B. 1,3-Dioxolan, 1-Octene, and Acetone with Ultraviolet Light.—The general procedure was followed employing 1-octene (8.84 g). The residue (16 g) remaining after the usual work-up was chromatographed on alumina to afford a mixture of telomers (1.45 g), 2-undecanone (0.1 g), and 2-octyl-1,3-dioxolan (3.7 g, 25%): bp 141–142° (40 mm); $n^{25}\mathrm{D}$ 1.4348 (lit.[24] bp 113.5–115° (17 mm); $n^{20}\mathrm{D}$ 1.4400); nmr, multiplets at 5.17 (1 H, $-OCHO-$) and 6.13 (4 H, $-OCH_2CH_2O-$), a broad signal at 8.7 (14 H, $-(CH_2)_7CH_3$), and a triplet at 9.1 (3 H, $-CH_2CH_3$). Treatment of the product with 2,4-dinitrophenylhydrazine reagent led to nonanal 2,4-dinitrophenylhydrazone, mp 100–101° (lit.[25] mp 100°). Later, 4-octyl-1,3-dioxolan (0.3 g, 2%), bp 130–132° (26 mm), $n^{19}\mathrm{D}$ 1.4371, was eluted: nmr, two sharp signals at 5.04 and 5.19 (2 H, $-OCH_2O-$), a multiplet at 6.04 (2 H, $-OCHCH_2O-$), an apparent triplet at 6.6 (1 H, C_8H_{17}-$CHO-$), a broad signal at 8.7 (14 H, $-(CH_2)_7CH_3$), and a triplet at 9.1 (3 H, $-CH_2CH_3$).

Anal. Calcd for $C_{11}H_{22}O_2$: C, 70.92; H, 11.90. Found: C, 70.80; H, 11.74.

Acid treatment of the product led to 1,2-decanediol, mp 45–47° (lit.[21] mp 48–49°). Finally were eluted 2-methyl-2-decanol (2.04 g), 2.2′-bi-1,3-dioxolan (0.2 g), and polar oils (2.4 g).

Anal. Found: C, 67.53; H, 11.43.

C. 1,3-Dioxolan, 1-Heptene, and Acetone with Ultraviolet Light.—The procedure described under A was followed using 7.74 g of 1-heptene. The residue (13 g) left after the usual work-up was chromatographed to yield a mixture of telomers (0.6 g), 2-decanone (0.4 g), and 2-heptyl-1,3-dioxolan (3.74 g, 27.6%): bp 115–116° (45 mm); $n^{25}\mathrm{D}$ 1.4318 (lit.[14] bp 117–119° (34 mm); $n^{30}\mathrm{D}$ 1.4292): nmr, a triplet at 5.17 (1 H, $-OCHO$), a multiplet at 6.14 (4 H, $-OCH_2CH_2O-$), a broad signal at 8.7 (12 H, $-(CH_2)_6CH_3$), and a triplet at 9.1 (3 H, $-CH_2CH_3$). The 2,4-dinitrophenylhydrazone of octanal, obtained as above, exhibited mp 102–103° (lit.[26a] mp 105.5°). Further elution gave 4-heptyl-1,3-dioxolan: yield, 0.7 g (5.2%); bp 112–114° (22 mm); $n^{19}\mathrm{D}$ 1.4332; nmr, two sharp signals at 5 and 5.15 (2 H, $-OCH_2O-$), a multiplet at 6.05 (2 H, $-OCHCH_2O-$), an apparent triplet at 6.6 (1 H, $C_7H_{15}CHO-$), a broad signal at 8.7 (14 H, $-(CH_2)_7CH_3)$), and a triplet at 9.1 (3 H, $-CH_2$-CH_3).

Anal. Calcd for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70. Found: C, 69.74; H, 11.56.

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[19] All boiling points and melting points are uncorrected. Merck "acid washed" alumina was used for chromatography unless otherwise stated. Gas–liquid partition chromatography (glpc) was carried out on an Aerograph A9OP instrument on a 20 ft × $\frac{3}{8}$ in. column of glass beads coated with 0.2% Apiezon L except for determination of isopropyl alcohol when a Carbowax 400 column was used. The nmr spectra were determined on a Varian A-60 instrument in $CDCl_3$ with TMS as an internal standard. The chemical shifts are given in τ values. Analyses were carried out in our microanalytical section directed by Mr. R. Heller.

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[26] (a) T. Malkin and T. C. Tranter, *J. Chem. Soc.*, 1178 (1951); (b) G. Bendz and M. Karth, *Acta. Chem. Scand.*, **11**, 903 (1957).

The compound was further characterized by treatment with dilute mineral acid leading to 1,2-nonanediol, mp 30–32° (*n*-pentane, refrigerator) (lit.[26b] mp 33.5–34°). Finally ethyl octanoate (0.3 g), 2-methyl-2-nonanol (2.6 g), and polar oils (4.78 g) were eluted.

Anal. Found: C, 65.95; H, 11.18.

D. 1,3-Dioxolan, 1-Dodecene, and Acetone with Ultraviolet Light.—The general procedure was followed using 11.37 g of 1-dodecene. The residue (17 g) left after the usual work-up was chromatographed on alumina and led to 1-dodecene (0.89 g), a mixture of telomers (0.2 g), 2-tridecanone (0.1 g), 2-dodecyl-1,3-dioxolan: yield, 5.7 g (34.8%); bp 108–110° (0.4 mm); $n^{21}\mathrm{D}$ 1.4448; nmr, multiplets at 5.17 (1 H, $\mathrm{O}\text{–}CH\text{–}\mathrm{O}$) and 6.13 (4 H, $\text{–}\mathrm{O}CH_2CH_2\mathrm{O}\text{–}$), a broad signal at 8.7 (22 H, $\text{–}(CH_2)_{11}\text{-}\mathrm{CH_3}$), and a triplet at 9.1 (3 H, $\text{–}\mathrm{CH_2}CH_3$).

Anal. Calcd for $C_{15}H_{30}O_2$: C, 74.32; H, 12.48. Found: C, 74.78; H, 12.36.

The 2,4-dinitrophenylhydrazone of tridecanal obtained by the usual procedure showed mp and mmp 104–105° (lit.[26a] mp 106.5°).

Further elution gave 4-dodecyl-1,3-dioxolan: yield, 1.1 g (6.7%); bp 104–105° (0.5 mm); $n^{20}\mathrm{D}$ 1.4450; nmr, two sharp signals at 5 and 5.1 (2 H, $\text{–}\mathrm{O}CH_2\mathrm{O}\text{–}$), a multiplet at 6.02 (2 H, $\text{–}\mathrm{OCH}CH_2\mathrm{O}\text{–}$) and apparent triplet at 6.53 (1 H, $\mathrm{C_{12}H_{25}}CH\mathrm{O}\text{–}$), a broad signal at 8.7 (22 H, $\text{–}(CH_2)_{11}\mathrm{CH_3}$), and triplet at 9.1 (3 H, $\text{–}\mathrm{CH_2}CH_3$).

Anal. Calcd for $C_{15}H_{30}O_2$: C, 74.32; H, 12.48. Found: C, 74.53; H, 12.42.

The compound was further characterized by treatment with dilute mineral acid leading to 1,2-tetradecanediol,[27] mp 65–66° (petroleum ether) (lit.[21] mp 68–68.5°). Finally were eluted 2-methyl-2-tetradecanol (4.33 g) and polar oils (2.26 g).

Anal. Found: C, 65.53; H, 11.32.

E. 1,3-Dioxolan, Methyl 10-Undecylenate, and Acetone with Ultraviolet Light.—The general procedure was followed employing 15.12 g of methyl 10-undecylenate. The usual method of work-up led to a residue (24 g) which was chromatographed on alumina to afford methyl 11-(1,3-dioxolanyl-2)-undecanoate: yield, 3.83 g (18.5%); mp 36–39° (petroleum ether); nmr, multiplets at 5.27 (1 H, $\mathrm{O}CH\mathrm{O}$) and 6.2 (4 H, $\text{–}\mathrm{O}(CH_2)_2\mathrm{O}\text{–}$), a singlet at 6.4 (3 H, $\text{–}\mathrm{COO}CH_3$), a multiplet at 7.8 (4 H, $\text{–}CH_2\text{–}$ from the chain, α to C_2, and $\text{–}CH_2\mathrm{COOCH_3}$), and a signal at 8.7 (16 H, $\text{–}(CH_2)_8\text{–}$).

Anal. Calcd for $C_{15}H_{28}O_4$: C, 66.14; H, 10.36. Found: C, 66.07; H, 10.37.

The 2,4-dinitrophenylhydrazone of methyl 11-formylundecanoate obtained as above showed mp 65–67° (lit.[28] mp 69–70°).

Further were eluted 2,2′-bi-1,3-dioxolan (0.2 g) and methyl 12-hydroxy-12-methyltridecanoate (0.71 g): bp 107–109° (0.7 mm); $n^{18}\mathrm{D}$ 1.4516; $\nu_{\max}^{\mathrm{neat}}$ 3400 and 1735 cm^{-1}.

Anal. Calcd for $C_{15}H_{30}O_3$: C, 69.72; H, 11.70. Found: C, 69.97; H, 11.86.

Alkaline hydrolysis of the compound led to 12-hydroxy-12-methyltridecanoic acid, mp 72–73° (petroleum ether–ether).

Anal. Calcd for $C_{14}H_{28}O_3$: C, 68.81; H, 11.55. Found: C, 68.62; H, 11.34.

Polar oils (2 g) were eluted with ether.

Anal. Found: C, 64.26; H, 10.32.

F. 1,3-Dioxolan, Methyl 4-Pentenoate, and Acetone with Ultraviolet Light.—Methyl 4-pentenoate (9 g) was used for this experiment. The usual method of work-up led to a residue (16 g) which was chromatographed on alumina to afford methyl 5-(1,3-dioxolanyl-2)-pentanoate: yield, 2.63 g (17.8%); bp 123–124° (5 mm); $n^{20}\mathrm{D}$ 1.4435; nmr, multiplets centered at 5.2 (1 H, $\text{–}\mathrm{O}CH\mathrm{O}\text{–}$) and 6.15 (4 H, $\text{–}\mathrm{O}CH_2CH_2\mathrm{O}\text{–}$), a singlet at 6.4 (3 H, $\text{–}\mathrm{COO}CH_3$), a multiplet at 7.7, and a broad signal at 8.45 (8 H, $\text{–}(CH_2)_4\mathrm{COOCH_3}$).

Anal. Calcd for $C_9H_{16}O_4$: C, 57.43; H, 8.57. Found: C, 57.43; H, 8.67.

The 2,4-dinitrophenylhydrazone of methyl 5-formylvalerate was obtained by the standard procedure and showed mp 101–103°.

Anal. Calcd for $C_{13}H_{16}O_6N_4$: C, 48.15; H, 4.97; N, 17.28. Found: C, 48.08; H, 5.01; N, 17.44.

Further elution gave the 4-alkyl isomer (0.3 g, 2%), 2.2′-bi-1,3-dioxolan (0.2 g), and methyl 6-hydroxy-6-methylheptanoate (0.9 g): bp 101–104° (7 mm); $n^{21}\mathrm{D}$ 1.4405.

Anal. Calcd for $C_9H_{18}O_3$: C, 62.04; H, 10.41. Found: C, 61.71; H, 10.25.

G. 1,3-Dioxolan, Diethyl Maleate, and Acetone with Ultraviolet Light.—A mixture of diethyl maleate (1 g), 1,3-dioxolan (110 ml), and acetone (10 ml) was irradiated for 1 hr. A solution of diethyl maleate (2.65 g) in acetone (5 ml) was then added in four equal portions at 1-hr intervals and the mixture was irradiated until consumption of diethyl maleate was complete (*ca.* 2 more hr after the last addition). The usual work-up led to a residue (6 g) which was chromatographed on silica gel.[29] Acetone–petroleum ether (1:9) eluted diethyl-(1,3-dioxolanyl-2)-succinate: yield, 4.59 g (87.5%); bp 120–125° (1.5 mm); $n^{25}\mathrm{D}$ 1.4457; nmr, a doublet at 4.81 (1 H, $\text{–}\mathrm{O}CH\mathrm{O}\text{–}$, $J = 4$ cps), two quartets ($J = 7$ cps) superimposed on a multiplet centered at 6 (8 H, $\text{–}\mathrm{O}CH_2CH_2\mathrm{O}\text{–}$ and ($\mathrm{O}CH_2\mathrm{CH_3}$), a multiplet centered at 6.82 (1 H, $\text{–}CH\mathrm{COOC_2H_5}$), a double doublet at 7.35 (2 H, $\text{–}CH_2\mathrm{COOC_2H_5}$), and a double triplet at 8.76 (3 H, $\text{–}\mathrm{CH_2}CH_3$, $J = 7$ cps).

Anal. Calcd for $C_{11}H_{18}O_6$: C, 53.65; H, 7.37. Found: C, 54.00; H, 7.36.

Treatment of the product with 2,4-dinitrophenylhydrazine reagent led to diethyl formylsuccinate 2,4-dinitrophenylhydrazone, mp 89–91°.

Anal. Calcd for $C_{15}H_{18}N_4O_8$: C, 47.12; H, 4.75; N, 14.66. Found: C, 46.97; H, 5.01; N, 14.86.

Alcohol–ether mixture eluted polar oils (1 g).

1,3-Dioxolan, Diethyl Maleate, and Acetophenone with Ultraviolet Light.—The reaction was carried out employing diethyl maleate (3.65 g), 1,3-dioxolan (110 ml), and acetophenone (8 ml). The usual work-up led to 4.6 g of unchanged acetophenone and 4.65 g (90%) of diethyl (1,3-dioxolanyl-2)-succinate.

1,3-Dioxolan and Diethyl Maleate with Ultraviolet Light.—A mixture of diethyl maleate (0.65 g) and 1,3-dioxolan (110 ml) was irradiated (quartz filter) for 1 hr. Diethyl maleate (3 g) was then added in four equal portions at 1-hr intervals. The mixture was irradiated for an additional 2 hr. The usual procedure of work-up led to 4.9 g (94%) of diethyl (1,3-dioxolanyl-2)-succinate. Under similar reaction conditions, but using a Pyrex filter, diethyl (1,3-dioxolanyl-2)-succinate was obtained in 7% yield.

H. 1,3,5-Trioxan, 1-Decene, and Acetone. 1. With Ultraviolet Light (at 65–70°).—A mixture of 1,3,5-trioxan (190 g), acetone (20 ml), and 1-decene (2 g) was irradiated for 1 hr. A solution of 1-decene (11 g) in acetone (10 ml) was then added in eight equal portions at 1-hr intervals and the mixture was further irradiated at the same temperature until consumption of the olefin was complete (*ca.* 28 hr). Excess reagents were removed under reduced pressure and the distillate was shown to contain 1,3,5-trioxan, acetone, and isopropyl alcohol (glpc, Carbowax 400 at 100°).

The residue (24 g) was chromatographed on alumina. Elution with petroleum ether–ether (9:1) gave an oil (0.77 g) believed to be a mixture of telomers. The same solvent mixture further eluted 2-tridecanone (2.5 g), followed by decyl-1,3,5-trioxan: yield, 4.5 g (21%); mp 43–44° (petroleum ether); nmr, multiplet centered at 4.9 (5 H, $\text{–}\mathrm{O}CH_2\mathrm{O}CH\mathrm{O}CH_2\text{–}$), a broad signal at 8.7 (18 H, $\text{–}(CH_2)_9\mathrm{CH_3}$), and a triplet at 9.1 (3 H, $\text{–}\mathrm{CH_2}CH_3$).

Anal. Calcd for $C_{13}H_{26}O_3$: C, 67.78; H, 11.38. Found: C, 68.33; H, 11.17.

Treatment of the product with 2,4-dinitrophenylhydrazine reagent led to a precipitate from which undecanal 2,4-dinitrophenylhydrazone was isolated by repeated recrystallizations. The 2,4-dinitrophenylhydrazone of formaldehyde could be detected by thin layer chromatography.

Ether–petroleum ether (4:1) eluted 2-methyl-2-dodecanol (5.15 g). Ether eluted bi-1,3,5-trioxan: yield, 0.9 g; mp 182–183° (petroleum ether); nmr, a multiplet centered at 4.8.

Anal. Calcd for $C_6H_{10}O_6$: C, 40.45; H, 5.66; mol wt, 178. Found: C, 40.68; H, 5.6; mol wt, 178.

Alcohol–ether mixture eluted polar oils (4.3 g).

Anal. Found: C, 66.10; H, 11.07.

When the reaction of 1,3,5-trioxan, 1-decene, and acetone

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(27) We are indebted to Professor D. Swern for a gift of 1,2-epoxytetradecane.

(28) H. Adkins and G. Krsek, *J. Am. Chem. Soc.*, **70**, 383 (1948).

(29) Products from the reactions of diethyl maleate with 1,3-dioxolan and 1,3,5-trioxan were separated by chromatography on Kieselgel 0.05–0.2 (Merck, Darmstadt).

(homogenized with *t*-butyl alcohol, see the reaction of methyl 10-undecylenate) was carried out at room temperature with ultraviolet light, decyl-1,3,5-trioxan was obtained in 15% yield.

2. In Sunlight.—A mixture of 1,3,5-trioxan (45 g), *t*-butyl alcohol (150 ml), acetone (25 ml), and 1-decene (1 g) was left in direct sunlight for 1 day. A solution of 1-decene (6.13 g) in acetone (5 ml) was then added in seven equal portions at 1-day intervals and the mixture was left in sunlight for another 9 days. Excess reagents were removed under reduced pressure and the residue (15 g) was chromatographed on alumina to yield a mixture of telomers (0.2 g), 2-tridecanone (1.95 g), decyl-1,3,5-trioxan (2.25 g, 19.5%), 2-methyl-2-dodecanol (2.22 g), and polar oils (4.94 g) from which bi-1,3,5-trioxan (0.3 g) could be isolated.

1,3,5-Trioxan, 1-Decene, and Acetophenone with Ultraviolet Light (at 65–70°).—The procedure described for the acetone-initiated reaction was followed using 1,3,5-trioxan (150 g), 1-decene (11.7 g), and acetophenone (10 g). The residue (30 g) obtained after the usual work-up was chromatographed on alumina to give a mixture of telomers (1.8 g), decyl-1,3,5-trioxan (4 g, 21%), acetophenone (0.1 g), and polar oils (20 g).

Anal. Found: C, 67.48; H, 10.78.

1,3,5-Trioxan, 1-Decene, and Benzophenone with Ultraviolet Light (at 65–70°).—The general procedure was followed employing the quantities used for the acetophenone-initiated reaction. The residue (25 g) left after the usual work-up was chromatographed on alumina to yield a mixture of telomers (0.8 g), decyl-1,3,5-trioxan (1.8 g, 9.4%), benzophenone (0.52 g), benzpinacol (4 g), and polar oils (10.9 g).

I. 1,3,5-Trioxan, 1-Octene, and Acetone. 1. With Ultraviolet Light (at 65–70°).—The general procedure was followed employing 1-octene (9.34 g). The residue (25 g) left after the usual work-up was chromatographed on alumina to afford a mixture of telomers (0.6 g), 2-undecanone (1 g), and octyl-1,3,5-trioxan (3.4 g, 20%): mp 30–31° (petroleum ether, refrigerator); nmr, a multiplet centered at 4.9 (5 H, $-OCH_2OCHOCH_2-$), a broad signal at 8.7 (14 H, $-(CH_2)_7CH_3$), and a triplet at 9.1 (3 H, CH_2CH_3).

Anal. Calcd for $C_{11}H_{22}O_3$: C, 65.31; H, 10.96. Found: C, 65.39; H, 10.72.

Treatment of the product with 2,4-dinitrophenylhydrazine reagent as above led to nonanal 2,4-dinitrophenylhydrazone and the 2,4-dinitrophenylhydrazone of formaldehyde. Further elution gave 2-methyl-2-decanol (3.1 g), bi-1,3,5-trioxan (2 g), and polar oils.

2. In Sunlight.—The general procedure for reactions in sunlight was followed and afforded octyl-1,3,5-trioxan (19%).

J. 1,3,5-Trioxan, 1-Heptene, and Acetone with Ultraviolet Light (at 65–70°).—The procedure described under H was followed using 8.16 g of 1-heptene. The residue (23.7 g) left after the usual work-up was chromatographed to yield a mixture of telomers (0.57 g), 2-decanone (0.7 g), and heptyl-1,3,5-trioxan (2.4 g, 15%): mp 22–24° (petroleum ether, refrigerator); nmr, a multiplet centered at 4.85 (5 H, $-OCH_2OCHOCH_2-$), a broad signal at 8.7 (12 H, $-(CH_2)_6CH_3$), and a triplet at 9.1 (3 H, $-CH_2CH_3$).

Anal. Calcd for $C_{10}H_{20}O_3$: C, 63.79; H, 10.71. Found: C, 64.29; H, 10.89.

Treatment of the product with a 2,4-dinitrophenylhydrazine reagent led to octanal 2,4-dinitrophenylhydrazone and formaldehyde 2,4-dinitrophenylhydrazone.

Further were eluted 2-methyl-2-nonanol (2.4 g), bi-1,3,5-trioxan (2 g), and polar oils (9 g).

When the reaction of 1,3,5-trioxan, 1-heptene, and acetone was carried out at room temperature (see L), heptyl-1,3,5-trioxan was obtained in 15% yield.

K. 1,3,5-Trioxan, 1-Dodecene, and Acetone with Ultraviolet Light (at 65–70°).—1-Dodecene (15 g) was employed in this experiment. The residue (31 g) left after the usual work-up was chromatographed on alumina and led to 1-dodecene (0.5 g), a mixture of telomers (0.54 g), 2-pentadecanone (0.9 g), mp 38–39° (petroleum ether, refrigerator) (lit.[30] mp 39°), 2,4-dinitrophenylhydrazone, mp 73–74° (lit.[31] mp 76.5°), followed by dodecyl-1,3,5-trioxan (5.44 g, 24%): mp 54–55° (petroleum ether); nmr, a multiplet centered at 4.9 (5 H, $-OCH_2OCHOCH_2$), a singlet at 8.7 (22 H, $-(CH_2)_{11}CH_3$), and a triplet at 9.1 (3 H, $-CH_2CH_3$).

Anal. Calcd for $C_{15}H_{30}O_3$: C, 69.72; H, 11.70. Found: C, 69.89; H, 11.51.

Treatment of the compound with a 2,4-dinitrophenylhydrazine reagent led to tridecanal 2,4-dinitrophenylhydrazone and formaldehyde 2,4-dinitrophenylhydrazone. Further elution gave 2-methyl-2-tetradecanol (3.37 g), bi-1,3,5-trioxan (2.4 g), and polar oils (10 g).

L. 1,3,5-Trioxan, Methyl 10-Undecylenate, and Acetone. 1. With Ultraviolet Light (at 65–70°).—The general procedure was followed employing 15 g of methyl 10-undecylenate. The usual method of work-up led to a residue (33 g) which was chromatographed on alumina to afford methyl 13-oxotetradecanoate (1 g), mp 40–41° (*n*-pentane) (lit.[6] mp 38–40°). The 2,4-dinitrophenylhydrazone showed mp and mmp 81–82° (ethanol). Further elution gave methyl 11-(1,3,5-trioxanyl)-undecanoate: yield, 4.1 g (19%); mp 58–59° (petroleum ether); nmr, a multiplet centered at 4.9 (5 H, $-OCH_2OCHOCH_2$), a singlet at 6.35 (3 H, $-OCH_3$), a multiplet centered at 7.75 (2 H, $-CH_2COOCH_3$), and a broad signal at 8.7 (18 H, $-(CH_2)_9CH_2-$).

Anal. Calcd for $C_{15}H_{28}O_5$: C, 62.47; H, 9.79. Found: C, 62.54; H, 9.71.

The 2,4-dinitrophenylhydrazone of methyl 11-formylundecanoate and formaldehyde 2,4-dinitrophenylhydrazone were obtained upon treatment of the product with a 2,4-dinitrophenylhydrazine reagent. Further were eluted methyl 12-hydroxy-12-methyltridecanoate (2.4 g), bi-1,3,5-trioxan (2.45 g), and polar oils.

Anal. Found: C, 63.88; H, 10.30.

1,3,5-Trioxan, Methyl 10-Undecylenate, and Acetone with Ultraviolet Light (at Room Temperature).—A mixture of 1,3,5-trioxan (45 g), dry *t*-butyl alcohol (150 ml), acetone (10 ml), and methyl 10-undecylenate (9.9 g) was irradiated by the usual procedure. Work-up led to a residue (23.1 g) which was chromatographed on alumina to give methyl 13-oxotetradecanoate (0.3 g), methyl 11-(1,3,5-trioxanyl)undecanoate (1.8 g, 12.5%), methyl 12-hydroxy-12-methyltridecanoate (2.14 g), bi-1,3,5-trioxan (2.78 g), and polar oils (7.5 g).

2. In Sunlight.—A mixture of 1,3,5-trioxan (45 g), *t*-butyl alcohol (150 ml), acetone (20 ml), and methyl 10-undecylenate (1 g) was left in direct sunlight for 1 day. A solution of methyl 10-undecylenate (8.9 g) and acetone (5 ml) was then added in seven equal portions at 1-day intervals and the mixture was left in sunlight for another 8 days. The usual work-up led to a residue (11 g) which was chromatographed on alumina to afford methyl 13-oxotetradecanoate (1.71 g), methyl 11-(1,3,5-trioxanyl) undecanoate (2.1 g, 14.5%), methyl 12-hydroxy-12-methyltridecanoate (1.27 g), and bi-1,3,5-trioxan (0.5 g).

M. 1,3,5-Trioxan, Methyl 4-Pentenoate, and Acetone with Ultraviolet Light (at 65–70°).—The general procedure was followed employing 9.5 g of methyl 4-pentenoate. The usual method of work-up led to a residue (12 g) which was chromatographed on alumina to afford an oil (0.05 g) which contained methyl 7-oxooctanoate (glpc) and methyl 5-(1,3,5-trioxanyl)-pentanoate: yield, 1.5 g (8.8%); mp 20–22°; nmr, multiplet centered at 4.9 (5 H, $-OCH_2OCHOCH_2-$), a sharp singlet at 6.38 (3 H, $-COOCH_3$), and multiplets centered at 7.7 (2 H, $-CH_2COOCH_3$) and 8.45 (6 H, $-(CH_2)_3-$).

Anal. Calcd for $C_9H_{16}O_5$: C, 52.93; H, 7.90. Found: C, 52.89; H, 8.02.

Treatment of the product with 2,4-dinitrophenylhydrazine reagent led to the 2,4-dinitrophenylhydrazones of methyl 5-formylvalerate and of formaldehyde. Bi-1,3,5-trioxan (2 g) was isolated from the polar oils (7.5 g) which were eluted later.

1,3,5-Trioxan, Methyl 4-Pentenoate, and Acetone with Ultraviolet Light (at Room Temperature).—A mixture of 1,3,5-trioxan (45 g), dry *t*-butyl alcohol (150 ml), acetone (10 ml), and methyl 4-pentenoate (5.7 g) was irradiated in the usual way. Work-up gave a residue (23 g) which by chromatography on alumina was separated into methyl 5-(1,3,5-trioxanyl)pentanoate (1 g, 9.8%), bi-1,3,5-trioxan (1.5 g), and polar oils.

N. 1,3,5-Trioxan, Diethyl Maleate, and Acetone with Ultraviolet Light (at 65–70°).—A mixture of 1,3,5-trioxan (150 g), acetone (10 ml), and diethyl maleate (1 g) was irradiated for 1 hr. A solution of diethyl maleate (3.3 g) in acetone (5 ml) was then added in four equal portions at 1-hr intervals and the mixture was irradiated until consumption of diethyl maleate was complete (*ca.* 2 hr). Excess reagents were removed under reduced pressure and the residue (10 g) was chromatographed on silica gel. Petroleum ether–acetone (3:1) eluted diethyl

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(30) P. Baumgarten, *Ber.*, **76**, 213 (1943).

(31) P. Z. G. Kramer and H. Van Duin, *Rec. Trav. Chim.*, **73**, 63 (1954).

(1,3,5-trioxanyl)succinate: yield, 1.74 g (26.6%); bp 140–145° (1 mm); $n^{18}\text{D}$ 1.4422; nmr, multiplet centered at 4.9 (5 H, $-OCH_2OCHOCH_2-$), two quartets at 5.8 and 5.9 (4 H, $-OCH_2CH_3$, J = 7 cps), multiplets centered at 6.8 (1 H, $-CHCOOC_2H_5$) and at 7.22 (2 H, $-CH_2COOC_2H_5$), and a triplet at 8.76 (6 H, $-CH_2CH_3$, J = 7 cps).

Anal. Calcd for $C_{11}H_{18}O_7$: C, 50.37; H, 6.92. Found: C, 50.67; H, 7.02.

The 2,4-dinitrophenylhydrazones of diethyl formyl succinate and of formaldehyde were obtained by the usual procedure. The same solvent mixture eluted bi-1,3,5-trioxan (1 g). Acetone–alcohol mixtures eluted polar oils.

1,3,5-Trioxan, Diethyl Maleate, and Acetophenone with Ultraviolet Light (at 65–70°).—The reaction was carried out with diethyl maleate (4.3 g), 1,3,5-trioxan (150 g), and acetophenone (8 ml). The usual work-up led to 5.4 g of unchanged acetophenone, 5.5 g (84%) of diethyl (1,3,5-trioxanyl)succinate, and polar oils (5.2 g).

Anal. Found: C, 52.68; H, 7.55.

1,3,5-Trioxan and Diethyl Maleate with Ultraviolet Light (at 65–70°).—A mixture of diethyl maleate (1 g) and 1,3,5-trioxan (150 g) was irradiated (quartz filter) for 1 hr. Diethyl maleate (3.3 g) was then added in three equal portions at 1-hr intervals and the mixture was irradiated for another 4 hr. The usual work-up led to diethyl (1,3,5-trioxanyl)succinate (1.5 g, 23%). Under similar reaction conditions, but using a Pyrex filter, diethyl (1,3,5-trioxanyl)succinate could not be detected.

Registry No.—2-Decyl-1,3-dioxolan, 6316-24-1; 4-decyl-1,3-dioxolan, 15138-46-2; 2,2′-bi-1,3-dioxolan, 6705-89-1; 2-octyl-1,3-dioxolan, 5432-30-4; 4-octyl-1,3-dioxolan, 15138-49-5; 2-heptyl-1,3-dioxolan, 4359-57-3; 2-dodecyl-1,3-dioxolan, 15138-51-9; 4-dodecyl-1,3-dioxolan, 15138-52-0; methyl 11-(1,3-dioxolanyl-2)undecanoate, 3515-98-8; methyl 12-hydroxy-12-methyltridecanoate, 15138-54-2; 12-hydroxy-12-methyltridecanoic acid, 15138-55-3; methyl 5-(1,3-dioxolanyl-2)pentanoate, 15138-56-4; methyl 5-formylvalerate 2,4-dinitrophenylhydrazone, 15138-57-5; methyl 6-hydroxy-6-methylheptanoate, 15188-17-7; diethyl (1,3-dioxolanyl-2)succinate, 15188-18-8; diethyl formylsuccinate 2,4-dinitrophenylhydrazone, 15188-19-9; decyl-1,3,5-trioxan, 14596-81-7; bi-1,3,5-trioxan, 15188-21-3; octyl-1,3,5-trioxan, 14596-80-6; heptyl-1,3,5-trioxan, 14596-79-3; dodecyl-1,3,5-trioxan, 15188-24-6; methyl 11-(1,3,5-trioxanyl)undecanoate, 15188-25-7; methyl 5-(1,3,5-trioxanyl)pentanoate, 15188-26-8; diethyl (1,3,5-trioxanyl)succinate, 15188-27-9.

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Compression Effects in 1,4-Di-*t*-butylnaphthalenes. Chemistry and Nuclear Magnetic Resonance Spectra[1]

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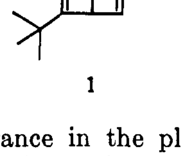
The syntheses of the 1,4-di-*t*-butylnaphthalenes **5**, **6**, **7**, **11**, **14**, and **15** are described. A compression effect of a *t*-butyl group in the acid-catalyzed rearrangement of endoxide **5** is detected. The effect is the addition of an external nucleophile to a benzcyclohexadienyl cation rather than the usual elimination of a proton to form a naphthalene. The air-sensitive naphthol **11** is examined for the possible presence of a ketone tautomer. The nmr spectra of the *peri* protons in the above compounds reveal a deshielding phenomenon attributed to a compression effect. An intramolecular nuclear Overhauser effect (NOE) is detected.

The effect of *t*-butyl crowding in benzenes has been examined in several ways. The stabilization of nonaromatic valence isomers, **1–3**, because of steric hindrance in the planar aromatic species is a striking result.[3] The change in the relative height of activation barriers in the steps of electrophilic aromatic substitution has been accomplished through a similar steric destabilization of the planar aromatic product.[4] An extension of the area of investigation to the potentially more crowded *peri*-*t*-butyl group in 1,4-di-*t*-butylnaphthalenes is described in this report.



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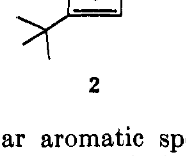

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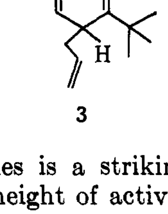

3

Our synthetic entry to the naphthalenes (Chart I) is *via* the aprotic diazotization of 2,5-di-*t*-butylaniline **4** in the presence of furan to afford 5,8-di-*t*-butyl-1,4-dihydronaphthalene-1,4-endoxide (**5**) in 21% yield.[5]

The structure of adduct **5** is based on its further conversions (*vide infra*) and on its very symmetrical nmr spectrum. The *t*-butyl protons at δ 1.30 and the aromatic protons at 6.77 were narrow singlets while the benzylic pair at 5.95 and the vinyl protons at 6.87 were identically shaped narrow multiplets indicative of an AA′BB′ system. Hydrogenation of endoxide **5** affords saturated endoxide **6** (97%). Dehydration with ethanolic hydrogen chloride yields 1,4-di-*t*-butylnaphthalene **7** in 94% yield. The richly

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[1] (a) Supported by the National Science Foundation, Grant GP 5160. (b) Parts of this research have been reported in preliminary form: Abstracts, Second Middle Atlantic Regional Meeting of the American Chemical Society, Feb 1967, p. 67; R. W. Franck and K. Yanagi, *Tetrahedron Letters*, 2905 (1966); R. W. Franck and K. Yanagi, *ibid.*, 1789 (1967).

[2] On leave from Research Institute of Science and Industry, Kyushu University, Fukuoka, Japan.

[3] (a) E. van Tamelen and S. Pappas, *J. Am. Chem. Soc.*, **84**, 3789 (1962), (b) K. Wilzbach and L. Kaplan, *ibid.*, **87**, 4004 (1965); (c) B. Miller, *ibid.*, **89**, 1685 (1967).

[4] (a) P. C. Myhre and M. Beug, *ibid.*, **88**, 1569 (1966); (b) E. Baciocchi, G. Illuminati, G. Sleiter, and F. Stegel, *ibid.*, **89**, 125 (1967).

[5] The detailed mechanism of this unusual reaction is the subject of a separate paper: K. Yanagi and R. W. Franck, manuscript submitted for publication.