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THE PHOTOALKYLATION OF CYCLIC ETHERS

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Abstract—The acetone, acetophenone and benzophenone-initiated photochemical alkylation of cyclic ethers with olefins is described. Alpha-alkylated cyclic ethers were obtained as the 1:1-adducts in yields of up to 40% with terminal olefins, and yields of up to 82% with α,β-unsaturated esters.

INTRODUCTION

THE free radical alkylation of both aliphatic and cyclic ethers with a variety of unsaturated substrates has recently attracted the attention of a number of research groups.[2–8] The direct alkylation of ethers with olefins involving radical intermediates serves as a useful synthetic method for the production of alkylated ethers. Ether free radicals have been reported to be relatively unstable at elevated temperatures and tend to undergo disproportionation which in the case of cyclic ethers results in decyclization of the ether ring.[9] Thus, some of the free radical alkylation reactions carried out at elevated temperatures may be unsuitable for the preparation of the alkylated ethers. This fact makes the photochemical addition reactions of increased value, since they are carried out at room temperature and the cyclic ether radicals produced under these conditions do not undergo ring decyclization.

The present study of the photoaddition of cyclic ethers to olefins[10] was undertaken with the aim of finding a general and simple process for the production of alkylated ether derivatives which might be applied to isolated olefinic bonds as well as to "activated" double bonds (i.e. α,β-unsaturated esters).

RESULTS

Cyclic ethers, such as tetrahydrofuran, tetrahydropyran and 1,4-dioxan were found to undergo a ketone-initiated photochemical addition to terminal olefins as well as to ethyl maleate and fumarate.[11] It has been shown[4,10] that this reaction can be induced directly by light or initiated photochemically by acetone, acetophenone or benzophenone, the latter cases furnishing higher yields of the 1:1-adducts. The 1:1-addition products obtained were the derived alpha-alkylated cyclic ethers. The

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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] [a] T. J. Wallace and R. J. Gritter, *Tetrahedron* **19**, 657 (1963); [b] T. J. Wallace, R. J. Gritter and H. G. Walsh, *Nature*, *Lond.* **198**, 284 (1963) and Ref cited therein.

[3] J. Diekmann and C. J. Pedersen, *J. Org. Chem.* **28**, 2879 (1963).

[4] R. L. Jacobs and G. G. Ecke, *J. Org. Chem.* **28**, 3036 (1963).

[5] N. I. Shuikin and B. L. Lebedev, *Izves. Akad. Nauk. SSSR. Ser. Khim.* 533 (1962).

[6] K. Yoshida and S. Tsutsumi, *Tetrahedron Letters* No. 28, 2417 (1965).

[7] M. J. Cziesla, K. F. Mueller and O. Jones, *Tetrahedron Letters* No. 8, 813 (1966).

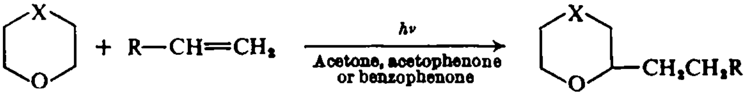
[8] R. C. Cookson, I. D. R. Stevens and C. T. Watts, *Chem. Commun.* **12**, 259 (1965).

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

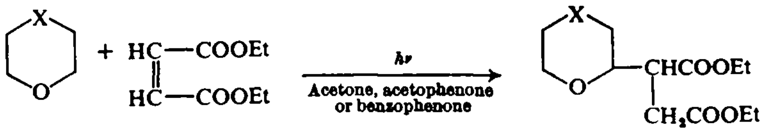
[10] For a preliminary note see D. Elad and R. D. Youssefyeh, *J. Org. Chem.* **29**, 2031 (1964).

[11] Since isomerization of the fumarate to the maleate takes place in the course of the reaction (see Ref 27), it is possible that addition of the cyclic ether to this system occurs exclusively through the maleate.

present paper includes full details of the reactions studied as well as their application to a variety of cases using different photoinitiators,[12] and a full description of the various products obtained. These reactions with terminal olefins and diethyl maleate or fumarate can be summarized as follows,



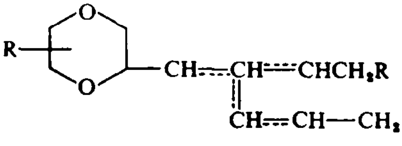
R = C_5H_{11}; C_6H_{13}; C_8H_{17}.



$X = \left[\begin{matrix} (CH_2)_n \\ n = 0 \text{ or } 1 \end{matrix}\right]$ or oxygen

The reactions investigated and the main products obtained are summarized in Table 1.

The 1:1-adducts were identified by means of their physical properties, elemental analyses, IR, NMR, and mass spectra, as well as by comparison with authentic samples. The esters were characterized similarly and were further hydrolysed to the corresponding dicarboxylic acids. Reaction products corresponding to addition compounds between an ether and more than one molecule of olefin (such as polysubstituted ethers and telomers) were obtained in lesser yields and identified by the same manner. Carbon–carbon unsaturation was detected in some of the telomers and resulted probably from disproportionation which is one of the possible termination steps of the assumed chain reaction (*vide infra*). Mass spectral determination of a telomeric product isolated from the reaction of 1,4-dioxan and 1-octene suggests the following partial structure,



(Molecular peak of *m/e* 422, and the following fragment-ion peaks at *m/e* 337, 309, 199, 87.)

Catalytic hydrogenation of this product on palladized charcoal gave the corresponding dihydro product which was characterized by means of its mass spectrum. (Molecular peak of *m/e* 424, and the following fragment-ion peaks at *m/e* 423, 339, 311, 199, 87.)

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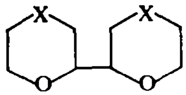
[12] The term "photosensitizer" (or sensitizer) is used in this article for a compound which initiates a photochemical process through light absorption and does not undergo a chemical change itself. The term "photoinitiator" is used for a compound which undergoes a chemical transformation while initiating a photochemical reaction.

TABLE 1. ADDITION PRODUCTS OF CYCLIC ETHERS AND UNSATURATED COMPOUNDS

Cyclic Ether	Olefin[a]	Product (1:1-adduct)	Yields (%)[b]		
			Acetone	Acetophenone	Benzophenone
Tetrahydrofuran	1-Heptene	2-Heptyltetrahydrofuran	17[c]; 35[d]		
	1-Octene	2-Octyltetrahydrofuran	20[c]		
	1-Decene	2-Decyltetrahydrofuran	18[c]; 38[d]		
	Diethyl Maleate	Diethyl Tetrahydrofuryl succinate	48[c]	80[c]; 80[d]	33[c]
Tetrahydropyran	1-Heptene	2-Heptyltetrahydropyran	16[c]		
	1-Octene	2-Octyltetrahydropyran	22[c]		
	1-Decene	2-Decyltetrahydropyran	24[c]		
	Diethyl Maleate	Diethyl Tetrahydropyranylsuccinate	16[c]	78[c]; 72[d]	53[c]
1,4-Dioxan	1-Heptene	Heptyl-1,4-dioxan	16[c]		
	1-Octene	Octyl-1,4-dioxan	26[c]; 41[d]	24[c]; 35[d]	14[c]
	1-Decene	Decyl-1,4-dioxan	34[c]		
	Diethyl Maleate	Diethyl 1,4-Dioxanylsuccinate	23[c]	73[c]	44[c]; 57[d]
	Diethyl Fumarate	Diethyl 1,4-Dioxanylsuccinate			46[c]

[a] The mole ratio of cyclic ether-olefin was 20:1 for terminal olefins and 45–75:1 for diethyl maleate and fumarate. [b] Based on the unsaturated compound employed. The conversions are nearly quantitative in most cases. [c] Hanau Q81 high pressure mercury vapour lamps were used as the radiation source for these reactions. [d] In sunlight.

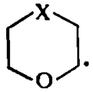
Dehydrodimers of the cyclic ethers having the following structure 

were obtained in these reactions. These compounds were characterized by elemental analysis, spectroscopic data and comparison with authentic samples.

Addition products of an acetone moiety (when used as initiator) and olefins were also isolated. These products were shown to be 2-methylalkanols-2 and methyl ketones, resulting from addition of an isopropanol and an acetonyl radical respectively.

These products were identified by their retention times in GLC and comparison of their solid derivatives with those of authentic samples.

DISCUSSION

The addition of cyclic ethers to terminal olefins can be induced directly by light or initiated photochemically by a ketonic compound. It seems that in the first case the ether radicals  generated in the mixture result from abstraction of a hydrogen atom from the ethers by other radicals formed during irradiation. The other possibility is that ether radicals are produced by hydrogen atom expulsion from an excited ether molecule; however this seems less probable, since saturated ethers absorb light of wavelengths shorter then 2000 Å.[13–18] The olefin serves as a scavenger for the cyclic ether radicals to give the alpha alkylated ethers. However, the concentration of the ether radicals produced by the direct light-induced reaction (quartz filtered) is probably low and yields of the alkylated ether obtained by this procedure are poor in the case of terminal olefins. In the acetone, acetophenone, and benzophenone-initiated reactions the consumption of olefins is faster and higher yields of the 1:1-adducts both with terminal olefins and diethyl maleate and fumarate were obtained.

Light filtered through Pyrex (wavelengths longer than 3000 Å) induced the acetone, acetophenone, and the benzophenone-initiated addition reactions in the case of terminal olefins, whereas in the absence of a ketone, no 1:1-addition products of the cyclic ether and the olefin could be detected under these reaction conditions. The ketonic compound here provides the main light absorbing system. The reaction presumably proceeds *via* excitation of the ketonic singlet–singlet transition decay to the carbonyl triplet which abstracts a hydrogen atom from the alpha-carbon of the cyclic ether to form a cyclic ether radical.[21] The possibility that the ether radicals result from the collapse of excited ether molecules which could be generated through energy transfer from the excited carbonyl compound seems less probable, since the triplet energies of ethers, though yet unknown,[22] are probably high in comparison with those of the ketones employed. This will make the process inefficient if at all possible. The isopropanol and the 2-methylalkanols-2 isolated from the reaction mixture when acetone was used as a photoinitiator, and the formation of considerable amounts of benzpinacol when benzophenone was employed (as well as 2,3-diphenylbutanediol-2,3 when acetophenone was employed), support the assumption of a hydrogen atom abstraction process.

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[13] L. W. Pickett, N. J. Hoeflich and T. C. Liu, *J. Am. Chem. Soc.* **73**, 4865 (1951).

[14] G. Scheibe and H. Grieneisen, *Z. Phys. Chem.* **B25**, 52 (1934).

[15] G. Fleming, M. M. Anderson, A. J. Harrison and W. Pickett, *J. Chem. Phys.* **30**, 351 (1959).

[16] A. J. Harrison and D. R. W. Price, *J. Chem. Phys.* **30**, 357 (1959).

[17] G. J. Hernandez, *J. Chem. Phys.* **38**, 2233 (1963).

[18] Photolyses of ethers in solution with light of wavelengths longer than 2000 Å have also been reported in the literature.[19,20] No explanations for these results have been given.

[19] K. Pfordte, *Liebigs. Ann.* **625**, 30 (1959).

[20] R. J. Gritter and E. C. Sabatino, *J. Org. Chem.* **29**, 1965 (1964).

[21] W. M. Moore, G. S. Hammond and R. P. Foss, *J. Am. Chem. Soc.* **83**, 2789 (1961).

[22] G. Porter: XIII-e Conseil de Chimie Solvay Report, Bruxelles, October 1965, p. 29.

The interaction of the excited ketonic photoinitiator with the olefins is a competitive process to the interaction of the former with the cyclic ethers and may serve as a quenching step. Though energy transfer processes from excited carbonyl compounds to isolated double bonds have been reported,[23-25] they do not seem to be very efficient, probably due to the "high" triplet energies of the olefinic compounds. In the present reaction, this process does not seem to interfere with the major reaction route when terminal olefins are employed. However, in the case of the α,β-unsaturated esters the energy transfer process from the excited carbonyl compound to the ester is pronounced and should be taken into consideration. In these cases it causes *cis-trans* isomerization of the maleate-fumarate system. Partially reacted mixtures always contained the two geometrical isomers, with a tendency to reach the photostationary state in which the maleate was the major component.[26,27] However, this quenching process of the initiation step could be overcome by adjusting the experimental conditions. Thus, the addition of the cyclic ethers to diethyl maleate or fumarate was effected with high yields while employing acetophenone as a photoinitiator. Results with acetone and benzophenone were less satisfactory.

The addition reaction of tetrahydrofuran and 1,4-dioxan to diethyl maleate could be effected without a photoinitiator while using the direct radiation of the source (quartz filter). However, when light of longer wavelengths (>3000 Å; Pyrex filters) was applied only the tetrahydrofuran addition reaction took place,[28] while no addition of 1,4-dioxan to the unsaturated ester could be detected under similar reaction conditions. The possibility of the formation of a charge transfer complex between tetrahydrofuran and diethyl maleate was examined, but no indication of additional or modified absorption was found.[29,30]

The experimental observations, i.e. the formation of (a) 1:1-adducts, (b) telomeric products, and (c) dehydrodimers of the ethers, seem to fit well into a free radical mechanism. The carbon–carbon unsaturation found in the telomeric product probably results from disproportionation of a radical as one of the possible chain termination steps. The 1:1-addition products of the cyclic ethers and terminal olefins isolated result from an anti-Markovnikov addition to the double bonds, i.e. the ether moiety adds to the terminal carbon. This may serve as another indication for the free radical nature of the reaction, being the characteristic orientation of addition of free radicals to terminal olefins.[31,32] Thus, the course of the reaction may be illustrated in

[23] G. S. Hammond, N. J. Turro and P. A. Leermakers, *J. Phys. Chem.* **66**, 1144 (1962).

[24] A. C. Testa, *J. Org. Chem.* **29**, 2461 (1964).

[25] R. E. Rebbert and P. Ausloos, *J. Am. Chem. Soc.* **87**, 5569 (1965).

[26] G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt and C. Dalton, *J. Am. Chem. Soc.* **86**, 3197 (1964).

[27] Cf. J. Rokach and D. Elad, *J. Org. Chem.* 31, 4210 (1966).

[28] Since saturated cyclic ethers absorb light of short wavelengths, it seems that the initial radicals formed during the direct light-induced reactions result from photolysis of impurities present in the cyclic ethers which could not be removed by the standard purification processes.

[29] Cf. C. E. H. Bawn, A. Ledwith and A. Parry, *Chem. Commun.* **20**, 490 (1965) and Refs cited therein.

[30] A. Cox, P. de Mayo and R. W. Yip, *J. Am. Chem. Soc.* **88**, 1043 (1966).

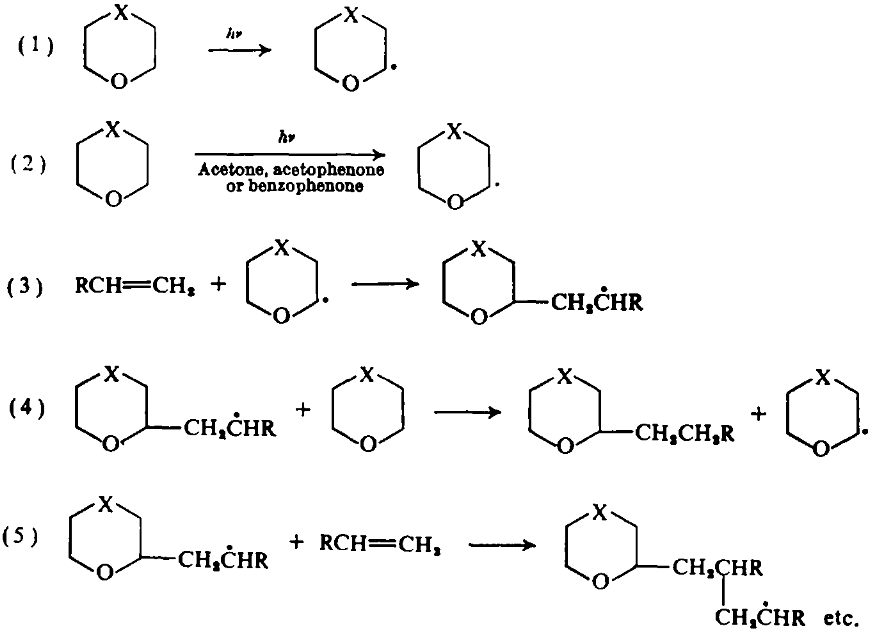
[31] Cf. C. Walling and E. S. Huyser, *Org. Reactions* **13**, 91 (1963) and Refs cited therein.

[32] An additional proof for the free radical nature of these reactions is the fact that some of them can be induced by peroxides under suitable reaction conditions.[2,5,33,34]

[33] Cf. W. E. Cass, *J. Am. Chem. Soc.* **69**, 500 (1947).

[34] Cf. C. S. Marvel, E. J. Prill and D. F. DeTar, *J. Am. Chem. Soc.* **69**, 52 (1947).

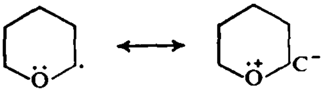
the following scheme:



Reactions 1 and 2 (direct light-induced or initiated photochemically with a ketone) are the initiation steps, whereas reactions 3 and 4 are the chain propagating steps to form 1:1-adducts. Reaction 5 leads to 2:1 and higher telomers.

Alpha substituted ethers were the only 1:1-adducts which were isolated from the reaction mixtures. Though substitution products at the beta and gamma positions of cyclic ethers have been reported in photochemical reactions[35] we could not detect the formation of the appropriate isomers in the cases studied. These isomers could be present as unseparated minor components of the peaks (GLC) containing the alpha substituted ethers. NMR data also were always consistent with a structure of alpha substituted cyclic ethers.

Cleavage of the potentially reactive alpha C—H bond in the cyclic ether molecule[36,37] leads to the formation of the corresponding alpha ether radicals which may derive their stabilization through resonance forms of the following type:



These radicals are probably nucleophilic and tend to give higher yields of the 1:1-adducts with α,β-unsaturated esters than with isolated terminal olefins.[31,38]

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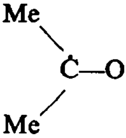
[35] E. Mueller and H. Huber, *Chem. Ber.* **96**, 2319 (1963).

[36] C. Walling, *Free Radicals in Solution* pp. 287, 412 and Refs. cited. Wiley, New York, N.Y. (1957).

[37] G. Sosnovsky, *Free Radical Reactions in Preparative Organic Chemistry* p. 370. Macmillan, New York, N.Y. (1964).

[38] Cf. G. H. Williams, *Progress in Stereochemistry* (Edited G. W. Kline and P. B. D. de la Mare) Vol. 2; p. 62.

The addition of acetone (when used as a photoinitiator) to olefins has been reported previously.[39] The 2-methylalkanols-2 result from the addition of the ketyl radical



$Me_2\dot{C}{-}OH$

to the olefin. These ketyl radicals are formed during the hydrogen atom abstraction process by the excited acetone molecule from the ether. The methyl ketones seem to be produced by a different species, i.e. the acetonyl radical, which adds to the olefin,[39]

$$RCH{=}CH_2 + \dot{C}H_2COCH_3 \rightarrow R\dot{C}HCH_2CH_2COCH_3$$

EXPERIMENTAL[40]

For general experimental details and description of irradiation apparatus see Elad and Rokach[37] and previous papers in the series. Typical experiments are described under A. Other experiments were carried out under similar conditions 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, 1966).

Reagents. The cyclic ethers were freshly distilled over Na before use; acetone, absolute acetophenone was freshly distilled before use; benzophenone, Fluka, was used without purification. The olefins were shaken with $FeSO_4$aq, dried (Na_2SO_4), and freshly distilled before use. Diethyl maleate and fumarate were freshly distilled before use.

Tetrahydrofuran, 1-heptene and acetone

(1) *With UV light.* A mixture of THF (110 ml), acetone (7 ml) and 1-heptene (0·5 g) was irradiated for 1 hr. A soln of 1-heptene (5·56 g) in acetone (7 ml) was then added in 8 equal portions at 1-hr intervals. The mixture was irradiated until complete consumption of the olefin (ca. 72 hr). Excess reagents were distilled at atm press on a steam bath and the distillate was shown to contain THF, acetone and isopropanol (2·5 g of isopropanol were detected by GLC on a carbowax 400 column at 100°). The 3,5-dinitrobenzoate derivative showed m.p. and mixed m.p. 121–122° (pet. ether). The remaining THF was removed under reduced press and the residue (19·5 g), the IR spectrum of which indicated only traces of carbonyl substances, was chromatographed on alumina. Elution with pet. ether gave an oil (0·2 g) believed to be a mixture of telomers. The same solvent further eluted 2-heptyltetrahydrofuran (1·8 g; 17%), b.p. 61–63° (2 mm), n_D^{26} = 1·4415 [lit.[41] b.p. 75° (8 mm) n_D^{20} = 1·4428].

NMR: multiplets centered at 6·15 (3H; $-CH_2{-}O{-}CH-$) and 8·1 (4H; ring-CH_2CH_2—beta to oxygen), a singlet at 8·7 (12H; $-(CH_2)_6CH_3$), and a triplet at 9·15 (3H; $-CH_2CH_3$). Ether-pet. ether (1:3) further eluted alpha bitetrahydrofuryl (0·9 g), b.p. 118–119° (30 mm) n_D^{25} = 1·4575 [lit.[42] b.p. 71°(10 mm) n_D^{20} = 1·4594]. NMR: two multiplets centered at 8 (8H; $-CH_2{-}CH_2-$ beta to oxygen) and 6·1 (6H; $-CH_2{-}O{-}CH{-}CH{-}O{-}CH_2-$). Mass spectrum: molecular peak of *m/e* 142 ($C_8H_{14}O_2$ requires: 142) and a fragment-ion peak at *m/e* 71. The compound was found to be identical with an authentic sample prepared.[42] 2-Methylnonanol-2 (2·3 g) was then eluted with

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[39] D. Elad and J. Rokach, *J. Org. Chem.* **29**, 1855 (1964).

[40] B.ps and m.ps are uncorrected. Merck "Acid Washed" alumina was used for chromatography in a ratio of 50:1. GLC was carried out on an Aerograph A 90 P with Speedomax G Recorder on a 20 feet × $\frac{3}{8}$ in column of glass beads coated with 0·2% Apiezon L at the temp stated. The NMR spectra were determined on a Varian A-60 spectrophotometer in $CDCl_3$ with TMS as an internal standard. The chemical shifts are given in τ values. Mass spectral determinations were carried on a MAT-Atlas CH4 instrument. Analyses were carried out in our microanalytical section directed by Mr. R. Heller.

[41] B. Notari, A. Ferretti and R. Onesta, *Gazz. Chim. Ital.* **89**, 1139 (1959), through *Chem. Abstr.* **54**, 22561 (1960).

[42] K. Shima and S. Tsutsumi, *Bull. Chem. Soc. Japan* **36**, 121 (1963).

the same solvent mixture. It was characterized by its retention time in GLC (at 150°), IR spectrum and the 3,5-dinitrobenzoate derivative, which exhibited m.p. and mixed m.p. 58–60° (pet. ether) (lit.[39] m.p. 58–60°). Glassy oils were eluted with ether-alcohol mixtures. (Found: C, 66·77; H, 11·46%.)

(2) *In sunlight.* A mixture of THF (110 ml), acetone (7 ml) and 1-heptene (0·5 g) was exposed to direct sunlight for 1 day. A soln. of 1-heptene (5·56 g) in acetone (7 ml) was then added in 7 equal portions at one-day intervals, and the mixture was left in direct sunlight for another 10 days until complete consumption of the olefin. Excess reagents were removed under reduced press and the residue (12 g) was chromatographed on alumina by the procedure described above to give a mixture of telomers (280 mg), 2-heptyltetrahydrofuran (3·7 g; 35%), 2-decanone, which was eluted with pet. ether and was found identical with an authentic sample (GLC and IR spectrum). The 2,4-dinitrophenylhydrazone derivative showed m.p. and mixed m.p. 72–74° (EtOH) (lit.[43] m.p. 73·5–74°). It was followed by 2-methylnonanol-2 (2·5 g) and glassy oils. (Found: C, 68·56; H, 11·65%.)

Tetrahydrofuran, 1-*octene and acetone with UV light*

The procedure described under A was followed using 7·59 g of 1-octene. The usual method of work-up led to a residue (11 g) which was chromatographed on alumina to yield a mixture of telomers (0·4 g), 2-octyltetrahydrofuran[19] (2·36 g; 19%), 2-undecanone (80 mg; GLC), 2-methyldecanol-2, and a glassy oil (3·5 g). The 2,4-dinitrophenylhydrazone of the ketone showed m.p. and mixed m.p. 62–64° (EtOD) (lit.[43] m.p. 64·5–65°). The 3,5-dinitrobenzoate of the tertiary alcohol exhibited m.p. and mixed m.p. 47–48° (pet. ether) (lit.[39] m.p. 47–48°).

Tetrahydrofuran, 1-*decene and acetone*

1. *With UV light.* The general procedure for irradiation with UV light was followed using 8·66 g of 1-decene. The residue (13·6 g) obtained by the usual work up was chromatographed on alumina to yield a mixture of telomers (1·2 g), 2-decyltetrahydrofuran (2·3 g; 18%), b.p. 89–90° (0·3 mm) n_D^{27} = 1·4479 [lit.[41] b.p. 138° (12 mm) n_D^{20} = 1·4498]. (Found: C, 79·07; H, 12·93. Calc. for $C_{14}H_{28}O$, C, 79·18; H, 13·29%.) NMR: multiplets centered at 6·15 (3H; $-CH_2-O-CH-$) and 8·1 (4H; ring $-CH_2-CH_2-$ beta to oxygen), a singlet at 8·7 (18H; $-(CH_2)_9-CH_3$) and a triplet at 9·15 (3H; $-CH_2CH_3$). Further eluted were alpha bitetrahydrofuryl (0·3 g), 2-methyldodecanol-2 (identical with an authentic sample) and polar glassy oils (6·4 g). (Found: C, 70·06; H, 11·96%.)

In sunlight. The reaction was carried out with 8·66 g of 1-decene. The usual method of work-up led to 2-decyltetrahydrofuran (5 g; 38%).

Tetrahydropyran, 1-*heptene and acetone with UV light*

The procedure described for THF was followed using tetrahydropyran (110 ml) and 1-heptene (5·35 g). The usual method of work-up gave a residue (10·7 g) which was chromatographed on alumina to give 2-heptyltetrahydropyran (1·6 g; 16%), b.p. 64–65° (0·3 mm), n_D^{27} = 1·4461 [lit.[44] b.p. 112° (12 mm)]. The compound was found identical with an authentic sample prepared according to Paul.[45] NMR: two multiplets centered at 6·1 and 6·7 (3H; CH_2-O-CH), a broad singlet centered at 8·65 (18H; all $-CH_2-$ except the methylene alpha to the ring oxygen), and a triplet centered at 9·15 (3H; $-CH_2-CH_3$). Further elution gave 2-decanone (GLC), 2-methylnonanol-2 (3 g), and polar glassy oils (3·1 g). (Found: C, 71·16; H, 12·58%.)

Tetrahydropyran, 1-*octene and acetone with UV light*

1-Octene (6·11 g) was used for this reaction. The usual work-up led to a residue (18·5 g) which was chromatographed on alumina to afford 2-octyltetrahydropyran[19] (2·4 g; 22%), 2-undecanone (GLC), 2-methyldecanol-2 (2·5 g) and polar oils. (Found: C, 71·94; H, 12·13%.)

Tetrahydropyran, 1-*decene and acetone with UV light*

1-Decene (7·64 g) was used for this reaction which after the usual work up led to a residue (11·5 g) containing 2-decyltetrahydropyran, (2·9 g; 24%), b.p. 91–92° (0·2 mm) n_D^{27} = 1·4479. (Found: C,

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[43] P. J. G. Kramer and H. Van Duin, *Rec. Trav. Chim.* **73**, 63 (1954).

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79·49; H, 13·03. $C_{15}H_{30}O$ requires: C, 79·57; H, 13·36%.) NMR: multiplets centered at 6·1 and 6·7 (3H; —CH_2—O—CH—), a broad singlet centered at 8·7 (24H; all —CH_2— except for the one alpha to the ring oxygen) and a triplet centered at 9·15 (3H; —CH_2CH_3). The oil (2·4 g) eluted next contained 2-tridecanone (GLC). The ketone gave a 2,4-dinitrophenylhydrozone derivative which showed m.p. and mixed m.p. 68–70° (EtOH). (lit.[45] m.p. 70–71°). 2-Methyldodecanol-2 (2·7 g) was eluted later and was shown to be identical with an authentic sample. Ether–EtOH mixtures eluted unidentified glassy oils (2·5 g) (Found: C, 72·36; H, 12·72%.)

1,4-*Dioxan*, 1-*heptene and acetone with UV light*

The general procedure was followed using 1,4-dioxan (115 ml) and 1-heptene (6·2 g). Work up led to a residue (7 g) which was chromatographed on alumina to give a mixture of telomers (1 g), heptyl-1,4-dioxan (1·9 g; 16%), m.p. 18–20° (n-pentane; refrigerator) (Found: C, 70·73; H, 11·32. $C_{11}H_{22}O_2$ requires: C, 70·92; H, 11·90%.) NMR: a multiplet centered at 6·4 (7H; —CH_2—CH_2—O—CH—CH_2—O—), a singlet at 8·7 (12H; —$(CH_2)_6$—CH_3), and a triplet at 9·1 (3H; —CH_2—CH_3). Mass spectrum: A molecular peak of $m/e = 186$ ($C_{11}H_{22}O_2$ requires: 186) and a fragment-ion of $m/e = 87$. Later were eluted 2-decanone (traces), 2-methylnonanol-2 (1·9 g), a mixture of dioxanyldioxan isomers[10,46] (0·9 g). NMR: a multiplet centered at 6·4.

1,4-*Dioxan*, 1-*octene and acetone*

(1) *With UV light*. 1-Octene (7·56 g) was used for this experiment. The usual procedure of work up indicated that the volatile fraction included acetone, dioxan and isopropanol (2·5 g; GLC). The 3,5-dinitrobenzoate of isopropanol showed m.p. and mixed m.p. 121–122° (pet. ether). The residue (14·7 g) was chromatographed on alumina to yield a mixture of telomers (0·7 g). One of the possible 3:1 dehydro-adducts of the olefin and 1,4-dioxan was isolated from this fraction in one experiment. (Found: C, 79·68; H, 12·78; mol.wt. 424. $C_{28}H_{54}O_2$ requires: C, 79·18; H, 13·29%; mol.wt: 424.) This product showed a carbon-carbon unsaturation and upon catalytic hydrogenation it was transformed to a 3:1-adduct (mol.wt. 426). Octyl-1,4-dioxan[10] (3·5 g; 26%) was eluted next and showed m.p. 37–38° (pet. ether). Later were eluted 2-undecanone, 2-methyldecanol-2 (500 mg), and a mixture of the isomeric dioxanyldioxans. One stereoisomer (0·4 g) showed m.p. 155–156° (pet. ether) and the other (0·4 g) exhibited m.p. 129–131° (pet. ether). (lit.[46] m.ps 157° and 132°, respectively). Ether–EtOH mixtures eluted a glassy oil (8 g). (Found: C, 61·96; H, 10·22%.)

(2) *In sunlight*. The general procedure using 5·6 g of 1-octene was followed. The usual method of work-up led to octyl-1,4-dioxan (4·1 g; 41%).

1,4-*Dioxan*, 1-*octene and acetophenone*

(1) *With UV light*. Acetophenone (12 g) was used according to the usual procedure. The residue (21·5 g) left after the usual work up was chromatographed on alumina to yield octyl-1,4-dioxan (2·7 g; 24%), acetophenone, a mixture of dioxanyldioxans (0·45 g), and polar oils (17 g) which showed an aromatic absorption in the IR and UV spectra. One spot in TLC had the same R_f value as 2,3-diphenylbutandiol-2,3.

(2) *In sunlight*. A mixture of dioxan (100 ml), 1-octene (6·21 g), and acetophenone (10 g) was left in direct sunlight. The usual method of work-up led to octyl-1,4-dioxan (3·86 g; 35%).

1,4-*Dioxan*, 1-*octene and benzophenone with UV light*

Benzophenone (10 g) was used for this experiment and the mixture was irradiated for 24 hr. Excess reagents were removed under reduced press and benzpinacol (3·4 g; m.p. 181–184°) was filtered off. The residue (16·8 g) left after evaporation of the solvent was chromatographed on alumina to yield octyl-1,4-dioxan (1·51 g; 14%).

1,4-*Dioxan*, 1-*decene and acetone with UV light*

The general procedure using 9·45 g of 1-decene was followed. The residue (16 g) was chromatographed on alumina to afford a mixture of telomers (1·65 g), decyl-1,4-dioxan (5·2 g; 34%), m.p. 45–46° (pet. ether) (Found: C, 73·59; H, 12·15. mol.wt. 228. $C_{14}H_{28}O_2$ requires: C, 73·63; H, 12·36%

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[46] G. Sosnovsky, *J. Org. Chem.* **28**, 2934 (1963).

mol. wt. 228). NMR: a multiplet centered at 6·35, (7H; —CH_2—CH_2—O—CH—CH_2—O—), a singlet at 8·7 (18H; —(CH_2)$_9$$CH_2$), and a triplet at 9·1 (3H; CH_2—CH_3). Mass spectrum: a molecular peak with *m/e* = 228 ($C_{14}H_{28}O_2$ requires 228) and a base peak with *m/e* = 87. Decyl-1,4-dioxan was contaminated with some 2-tridecanone (GLC). Later were eluted 2-methyldodecanol-2 (4 g), a mixture of dioxanyldioxan isomers (2·3 g), and polar oils (3 g). (Found: C, 77·95; H, 12·98%.)

Tetrahydrofuran, diethyl maleate and acetone with UV light

A mixture of diethyl maleate (1 g) THF (110 ml) and acetone (5 ml) was irradiated[47] for 1 hr. A soln of diethyl maleate (4 g) in acetone (5 ml) was then added in 8 equal portions at 1-hr intervals, and the mixture was irradiated until complete consumption of diethyl maleate (about 20 hr). Excess reagents were removed under reduced press, and the residue (9 g) was chromatographed on alumina. Ether–pet. ether (1:1) eluted alpha bitetrahydrofuryl (0·7 g). The same solvents mixture further eluted diethyl alphatetrahydrofurylsuccinate (3·4 g; 48%) b.p. 108–109° (0·2 mm) n_D^{27} = 1·4490 [lit.[48] b.p. 122–131° (1–2 mm), $n_D^{24\cdot5}$ = 1·4511]. (Found: C, 58·83; H, 7·93; Calc. for $C_{12}H_{20}O_5$: C, 59·00; H, 8·25%.) NMR: multiplets centered at 5·9 (7H; —CH_2—O—CH in the ring and —O—CH_2—CH_3), 7·3 (3H; —CH($COOC_2H_5$)—CH_2—$COOC_2H_5$), and 8·1 (4H; ring—CH_2—CH_2— beta to oxygen), and in triplet at 8·75 (3H; —CH_2—CH_3). Mass spectrum exhibited prominent peaks at *m/e* 199, 174, 157, 129, 128, 100, 71, 70. The peak having the highest *m/e* value corresponds to an ion which results from an expulsion of an ethoxy radical from one of the ester groups. The other peaks were obtained by the usual fragmentation processes.

It is noteworthy that similar peaks were obtained in the mass spectral determinations of the diesters resulting from addition of tetrahydropyran and dioxan to diethyl maleate and fumarate (*vide infra*).

Alkaline hydrolysis of the product led to alpha-tetrahydrofurylsuccinic acid, m.p. 143–144° (acetone–pet. ether) [lit.[49] m.p. 136–137°]. (Found: C, 50·73; H, 6·47. $C_8H_{12}O_5$ requires: C, 51·06; H, 6·43%.) NMR (D_2O): multiplets at 6·2 (3H; —CH—O—CH_2—), 7·3 (3H; —CH(COOH)—CH_2—COOH) and 8·21 (4H; ring —CH_2—CH_2— beta to oxygen). Ether and EtOH–ether mixtures eluted unidentified polar oils. (Found: C, 58·46; H, 8·44%.)

Tetrahydrofuran, diethyl maleate and acetophenone

(1) *With UV light.* The reaction was carried out with diethyl maleate (5 g) THF (110 ml) and acetophenone (5 g). The usual work up led to 0·79 g of unchanged acetophenone and 5·7 g (80%) of diethyl alpha-tetrahydrofurylsuccinate.

(2) *In sunlight.* A mixture of THF (110 ml), acetophenone (2·5 ml) and diethyl maleate (1 g) was left in direct sunlight for 1 day. A soln of diethyl maleate (4 g) in acetophenone (2·5 ml) was then added in 4 equal portions during 2 days and the mixture was left in direct sunlight for another day. Excess reagents were removed under reduced press and the residue (15 g) was chromatographed on alumina. Ether–pet. ether (1:1) eluted acetophenone (1·4 g) followed by crude diethyl alpha-tetrahydrofurylsuccinate (5·7 g; 80%).

Tetrahydrofuran, diethyl maleate and benzophenone with UV light

Benzophenone (5 g) was used for this experiment. Work up led to 1·5 g of unchanged benzophenone followed by a mixture of benzpinacol and diethyl alpha-tetrahydrofurylsuccinate. Benzpinacol (1·1 g) was removed by repeated treatment of the mixture with boiling pet. ether. Diethyl alpha-tetrahydrofurylsuccinate (2·3 g; 32%) was purified by distillation.

Tetrahydrofuran and diethyl maleate with UV light

(a) A mixture of diethyl maleate (1 g) and THF was irradiated (quartz filter) for 1 hr. Diethyl maleate (4·03 g) was then added in 4 equal portions at 1-hr intervals. The mixture was irradiated for 48 hr. The usual work up led to recovered diethyl maleate (0·2 g) and diethyl alpha tetrahydrofurylsuccinate (3·5 g; 49·1%).

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[47] "Sovirel" glass filter was used for the experiments of diethyl maleate and fumarate with acetone. It was found that this glass is more transparent to light than Pyrex glass at the 2700–3000 Å region.

[48] G. G. Ecke and R. L. Jacobs, US 3.114.752, through *Chem. Abstr.* **60**, 6827 (1964).

[49] A. Ledwith and M. Sambhi, *J. Chem. Soc.* (B) 670 (1966).

(b) The same experiment with a Pyrex filter and 20 hr irradiation led to recovered diethyl maleate (3·38 g) and diethyl alpha-tetrahydrofurylsuccinate (2·3 g; 32·4%).

Tetrahydropyran, diethyl maleate and acetone with UV light

A mixture of diethyl maleate (0·5 g) tetrahydropyran (110 ml) and acetone (7 ml) was irradiated for 1 hr. A mixture of diethyl maleate (2·5 g) and acetone (5 ml) was then added in 8 equal portions, at 1-hr intervals, and the mixture was further irradiated for 3 hr. Excess reagents were removed under reduced press and the residue (6·2 g) was chromatographed. Ether–pet. ether (1:1) eluted alpha-bitetrahydropyranyl (0·4 g). b.p. 148–150 (30 mm) $n_D^{28} = 1·4601$. (Found: C, 70·17; H, 11·07. $C_{10}H_{18}O_2$ requires, C, 70·54; H, 10·66%.) NMR: two multiplets centered at 6 and 6·65 (6H; —CH_2—O—CH—CH—O—CH_2—) and a broad singlet centered at 8·45 (12H; —CH_2— beta and gamma to oxygen). Mass spectrum: a molecular peak of *m/e* 170 ($C_{10}H_{18}O_2$ requires 170) and a base peak of *m/e* 85). The same solvent mixture further eluted diethyl alpha-tetrahydropyranylsuccinate (0·7 g; 15·5%), b.p. 135–137° (0·2 mm), $n_D^{25} = 1·4590$. (Found: C, 59·98; H, 8·68; $C_{13}H_{22}O_5$ requires: C, 60·44; H, 8·59%). NMR: a quartet superimposed on a multiplet centered at 5·8 and a multiplet centered at 6·55 (7H; —CH_2—O—CH— and O—$CH_2\mathrm{CH_3}$), a multiplet centered at 7·75 (3H; CH—($\mathrm{COOC_2H_5}$)—CH_2—$\mathrm{COOCH_2CH_3}$), and a triplet superimposed on a wide singlet centered at 8·55 (12H; ring methylenes beta and gamma to oxygen and —$\mathrm{CH_2}$—CH_3). Mass spectrum exhibited prominent peaks at *m/e*: 213, 174, 171, 129, 128, 100, 85, 84.

Alkaline hydrolysis of the product led to alpha-tetrahydropyranylsuccinic acid, m.p. 140–141° (pet. ether–AcOEt). (Found: C, 53·64; H, 6·94; $C_9H_{14}O_5$ requires: C, 53·46; H, 6·98%.) NMR: (D_2O): a broad band centered at 6·2 (3H; —CH_2—O—CH—), a multiplet centered at 7·2 (—CH(COOH)—CH_2—COOH), and a broad singlet at 8·4 (6H; ring methylenes beta and gamma to oxygen). EtOH–ether mixtures eluted polar oils (3·5 g). (Found: C, 58·86; H, 8·18%.)

Tetrahydropyran, diethyl maleate and benzophenone with UV light

The general procedure was followed using 5 g of benzophenone. The usual work up led to recovered benzophenone (1·5 g), benzpinacol (2 g), and diethyl alpha-tetrahydropyranylsuccinate (2·4 g; 53%). The latter products were separated by continuous treatment with pet. ether.

Tetrahydropyran, diethyl maleate and acetophenone

(1) *With UV light.* Acetophenone (10 g) was used for this experiment which led to recovered acetophenone (5·6 g) and diethyl alpha-tetrahydropyranylsuccinate (3·5 g; 78%).

(2) *In sunlight.* Work-up gave a residue (13 g) containing acetophenone (5 g), diethyl alpha-tetrahydropyranylsuccinate (3·2 g; 71%), and polar glassy oils (3 g).

Tetrahydropyran and diethyl maleate

A mixture of diethyl maleate (1 g) and tetrahydropyran (110 ml) was irradiated (quartz filter) for 1 hr. Diethyl maleate (4·03 g) was then added in 4 equal portions at 1-hr intervals. The mixture was irradiated for 48 hr. The usual work-up led to recovered diethyl maleate (0·2 g), diethyl alpha-tetrahydropyranylsuccinate (2·3 g; 30% yield).

1,4-*Dioxan, diethyl maleate and acetone with UV light*

A mixture of diethyl maleate (3 g), 1,4-dioxan (110 ml) and acetone (12 ml) was employed. The residue (7·3 g) left after the usual work up was chromatographed on alumina. Ether–pet. ether (1:3) first eluted 0·2 g of dioxanyldioxans, followed by diethyl 1,4-dioxanylsuccinate (1·1 g; 23%), b.p. 178–179° (0·2 mm), $n_D^{24} = 1·4511$ (Found: C, 55·24; H, 7·75; $C_{12}H_{20}O_6$; requires: C, 55·37; H, 7·75%). NMR: multiplets centered at 6·2 (11H; 1,4-dioxan protones and —O—CH_2—$\mathrm{CH_3}$) and 7·2 (3H; CH($\mathrm{COOC_2H_5}$)—$CH_2\mathrm{COOC_2H_5}$), and a triplet centered at 8·75 (6H; —O—$\mathrm{CH_2}$—CH_3). Mass spectrum exhibited peaks at *m/e*: 215, 174, 173, 129, 128, 100, 87, 86. Alkaline hydrolysis of the product led to 1,4-dioxanylsuccinic acid, m.p. 123–124° (pet. ether–AcOEt) (lit.[24] m.p. 126–128°) NMR (D_2O): multiplets centered at 6·2 (7H; —CH—O—CH_2—CH_2—O—CH_2—) and 7·15 (3H; —CH—(COOH)—CH_2—COOH).

When a Pyrex filter was employed instead of "Sovirel", diethyl 1,4-dioxanylsuccinate was obtained in 11% yield.

1,4-*Dioxan, diethyl maleate and acetophenone with UV light*

Acetophenone (10 g) was used for this experiment. Work up and chromatography led to recovered acetophenone (5·75 g), dioxanyldioxans (0·1 g), diethyl dioxanylsuccinate (3·3 g; 73%), and polar oils.

1,4-*Dioxan, diethyl maleate and benzophenone*

(1) *With UV light.* The general procedure was followed using 7 g of benzophenone. The usual work up afforded recovered benzophenone (2·4 g), benzpinacol (1·2 g), and a mixture of diethyl 1,4-dioxanylsuccinate, dioxanyldioxan and benzpinacol. Repeated treatments of the mixture with ether–pet. ether separated the solid from the liquid (2 g; 44%) which was shown to be diethyl 1,4-dioxanylsuccinate.

(2) *In sunlight.* Benzophenone (7 g) and 3 g of diethyl maleate were employed. The residue (15·8 g) obtained after work up was chromatographed on alumina to yield benzophenone (1·5 g), benzpinacol (2·5 g), diethyl 1,4-dioxanylsuccinate (2·6 g; 57%), and polar glassy oils (5 g).

1,4-*Dioxan and diethyl maleate*

A mixture of diethyl maleate (1 g) and 1,4-dioxan (110 ml) was irradiated for 1 hr (quartz filter). Diethyl maleate (4·03 g) was then added in 4 equal portions at 1-hr intervals. The mixture was irradiated for 48 hr. Work up led to recovered diethyl maleate (0·6 g) and diethyl 1,4-dioxanylsuccinate, (1 g; 13% yield). Under similar reaction conditions while using a Pyrex filter no diethyl 1,4-dioxanylsuccinate could be detected.

1,4-*Dioxan, diethyl fumarate and benzophenone with UV light*

A mixture of diethyl fumarate (1 g), 1,4-dioxan (110 ml) and benzophenone (7 g) was irradiated for 1 hr. Samples were taken out at 10 min intervals and the composition of the unreacted ester was determined by GLC. (Apiezon L column at 120°) and showed the following results:

Time (min)	Maleate (%)
10	ca. 2
25	10
40	40
60	95

Diethyl fumarate (2 g) was then added at 1-hr intervals. The mixture was irradiated until complete consumption of the ester (about 11 hr). Excess reagents were removed under reduced press and the residue (17·7 g) was chromatographed on alumina. Ether–pet. ether (1:1) eluted benzophenone (4·7 g); the same solvent mixture (3:1) further eluted a mixture of benzpinacol (1·1 g) and diethyl 1,4-dioxanylsuccinate (2·1 g; 46%), which were separated upon treatment with pet. ether. EtOH–ether mixtures eluted polar oils (2·5 g).

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