

**The Photocycloaddition of Various Ketones and Aldehydes  
to Vinyl Ethers and Ketene Diethyl Acetal<sup>1</sup>**

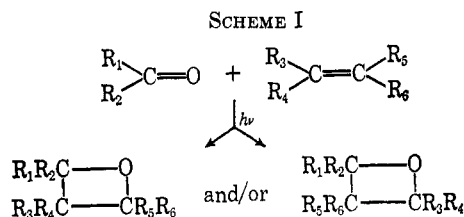
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Photoaddition of acetone to ethyl, *n*-butyl, and isobutyl vinyl ether and of propionaldehyde, cyclohexanone, benzaldehyde, and benzophenone to ethyl vinyl ether gives the corresponding 2- and 3-alkoxyoxetanes in ratios of  $(25 \pm 5):75$  independent of solvent. Acetone, cyclohexanone, and benzophenone also add to ketene diethyl acetal to give 2,2- and 3,3-diethoxyoxetanes in analogous ratios. Only 3,3-dialkoxyoxetanes were obtained from the photochemical reaction of ketene diethyl acetal with propion- and benzaldehyde. Selective transformations of 2-alkoxy- and 2,2-dialkoxyoxetanes with water, alcohols, or lithium aluminum hydride are used as a means of analyzing the reaction mixtures. The directions of the cycloadditions are compared with those of radical additions to vinyl ethers and ketene acetals. It is concluded that the isomer ratios in the cycloadditions cannot simply be predicted from the energy differences of the possible intermediates.

The Paterno-Büchi reaction, *i.e.*, the photocycloaddition of ketones and aldehydes to olefins, has recently been the subject of considerable study. Preparative work has been concerned with variations of the carbonyl<sup>2-4</sup> as well as of the olefinic<sup>5,6</sup> components. Mechanistic studies have shown that the cycloaddition to electron-rich olefins occurs *via* the  $n-\pi^*$  triplet state of the carbonyl compounds<sup>7-9</sup> and that the addition follows a two-step mechanism, *cis* and *trans* olefins giving the same mixtures of stereoisomeric oxetanes.<sup>10</sup> Rationalization of the mode



of cycloaddition to unsymmetrical substituted olefins<sup>11</sup> has also led to the postulation of a nonconcerted mechanism; the predominant isomer formed is correctly predicted from consideration of the more stable biradical (ground state) intermediate, formed by addition of the carbonyl oxygen to the carbon-carbon double bond<sup>11</sup> (Scheme I).

This paper describes the photocycloaddition of carbonyl compounds to vinyl ethers and to ketene diethyl acetal. The reaction represents a facile synthesis of mono- and dialkoxyoxetanes—compounds of considerable synthetic interest.<sup>12</sup> The quantitative determination of the isomer ratios formed from both vinyl ethers and ketene acetal has permitted a comparison of the direction of addition in both systems. The results show that product ratios are not always simply predicted from the stability of the intermediate radicals.

**Results**

**Vinyl Ethers.**—Acetone, propionaldehyde and cyclohexanone, when irradiated in the  $n-\pi^*$  region of the

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(4) (a) S. Farid and K.-H. Scholz, *ibid.*, 412 (1968); (b) S. Farid, D. Hess, and C. H. Krauch, *Chem. Ber.*, 100, 3266 (1967); (c) C. H. Krauch and S. Farid, *ibid.*, 100, 1685 (1967); (d) C. H. Krauch, S. Farid, and G. O. Schenek, *ibid.*, 98, 3102 (1965); (e) C. H. Krauch and S. Farid, *Tetrahedron Lett.*, 4783 (1966).

(5) (a) D. R. Arnold and A. H. Glick, *Chem. Commun.*, 813 (1966); (b) H. Gotthardt, R. Steinmetz, and G. S. Hammond, *ibid.*, 480 (1967); *J. Org. Chem.*, 33, 2774 (1968).

(6) (a) S. Toki and H. Sukurai, *Tetrahedron Lett.*, 4119 (1967); (b) G. R. Evanega and E. B. Whipple, *ibid.*, 2163 (1967); (c) J. Leitich, *ibid.*, 1937 (1967); (d) M. Ogata, H. Watanabe, and H. Kanō, *ibid.*, 533 (1967); (e) C. Rivas and E. Payo, *J. Org. Chem.*, 32, 2918 (1967).

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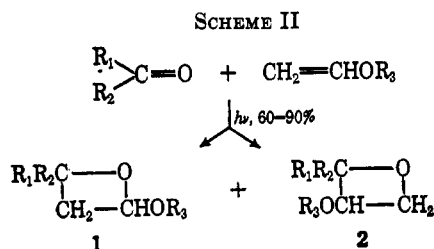
(8) L. A. Singer and G. A. Davis, *ibid.*, 89, 598, 158 (1967).

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(10) N. J. Turro, P. Wriede, J. C. Dalton, D. Arnold, and A. Glick, *J. Amer. Chem. Soc.*, 89, 3950 (1967).

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carbonyl group, readily added to vinyl ethers to afford mixtures of 2- and 3-alkoxyoxetanes (1 and 2, respectively) in high conversions and good yields (50–70%). With a 450-W medium-pressure mercury lamp, 50–60 g of oxetanes could be prepared within 24 hr. Similar high conversions and even better yields (80–90%) were obtained from the irradiation of benzaldehyde and benzophenone with vinyl ethers (Scheme II).

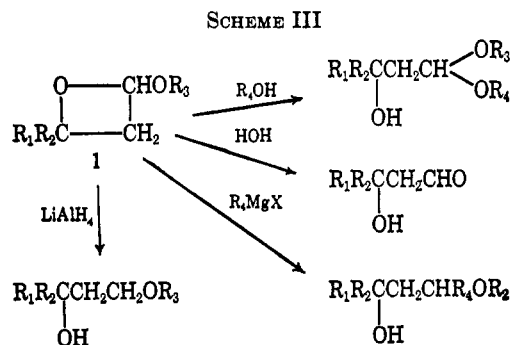
In many cases, the ratio of 2- to 3-alkoxyoxetanes could be determined by nmr spectroscopy. 2-Alkoxyoxetanes such as 1 show an ABX spectrum for their ring protons; the signal for the proton  $\alpha$  to the ring oxygen (X part) appears around  $\tau$  4.8, those for the  $\beta$  protons (AB part) appear at *ca.*  $\tau$  7.5. 3-Alkoxyoxetanes, on the other hand, display an ABC pattern around  $\tau$  5.5. Integration over these signals gave the relative amounts of isomers. In addition, gas chromatographic analysis of the reaction mixtures was also possible in many cases. Results obtained from the gas chromatographic and nmr analyses were usually in good agreement (Table I). The mixtures obtained from the addition of benzaldehyde or benzo-

TABLE I  
PRODUCT COMPOSITION OF ALKOXYOXETANES FROM  
THE PHOTOCHEMICAL CYCLOADDITION OF CARBONYL COMPOUNDS  
TO VINYL ETHERS<sup>a</sup>

Carbonyl compound	Ether	Yield, <sup>b</sup> %	2:3 <sup>d</sup>	
			Vpc	Nmr
Acetone	Ethyl vinyl	60–70 <sup>c</sup>	30:70	25:75
Acetone	<i>n</i> -Butyl vinyl	60	25:75	25:75
Acetone	Isobutyl vinyl		25:75	
Propionaldehyde	Ethyl vinyl	49	19:81 <sup>e</sup>	16:84
Cyclohexanone	Ethyl vinyl	50	30:70	30:70
Benzaldehyde	Ethyl vinyl	85	30:70 <sup>e</sup>	
Benzophenone	Ethyl vinyl	99	25:75 <sup>e</sup>	

<sup>a</sup> Irradiations in excess vinyl ether as a solvent; for solvent effects, see Table IV. <sup>b</sup> Yields after distillation. <sup>c</sup> Based on consumed ethyl vinyl ether; if calculated for consumed acetone, yields are much higher. Yields depend on irradiation conditions, 60% were obtained with Vycor, 70% with Corex filters. <sup>d</sup> Isomer ratios accurate to within  $\pm 5\%$ . <sup>e</sup> After alcoholysis, see text.

phenone to ethyl vinyl ether and butyl vinyl ether could not be analyzed in the described manner because of overlap of nmr signals and decomposition of the compounds on vpc analysis. It was possible, however, to determine the isomer ratios in an indirect way *via* selective chemical transformations of the 2-alkoxy isomers. As described in detail in an accompanying paper,<sup>12</sup> 2-alkoxyoxetanes were found to react quantitatively with water, alcohols, phenols, Grignard reagents and lithium aluminum hydride under conditions where 3-alkoxyoxetanes are inert (Scheme III). Vpc analysis of these reaction mixtures permitted an indirect determination of the original product com-



positions. The isomer ratios obtained in all these additions are collected in Table I.

The reaction of the carbonyl compounds with the vinyl ethers always gave higher boiling materials together with an undistillable residue as side products. The observed ratios of 3- to 2-alkoxyoxetanes will, of course, only represent the original compositions if these higher molecular weight products are not formed preferentially from one of the isomers. Since the same isomer ratio was observed in all cases, including those where little polymeric material was formed, it is felt that the ratios given in Table I do indeed represent the original compositions. Further support for this comes from the observation that the isomer ratio was found to be unchanged during irradiation and that it was the same regardless of whether quartz, Pyrex, or Corex vessels were employed. The use of different filters only effected the amount of higher molecular weight materials formed. These materials were shown to consist mainly of vinyl ether units.

No solvent effects have been observed in the cycloadditions. The ratio of isomers formed was virtually unchanged in either neat vinyl ether or in benzene, acetonitrile or *t*-butyl alcohol (Table II). Addition

TABLE II  
PRODUCT COMPOSITIONS FROM THE PHOTOCYCLOADDITION  
IN DIFFERENT SOLVENTS

Carbonyl compound	Amt. mol/l.	Ether	Amt. mol/l.	Solvent	Quencher	2 isomer, %
Ph <sub>2</sub> CO	0.1–0.3	EVE <sup>a</sup>	Neat			23 $\pm$ 3
Ph <sub>2</sub> CO	0.1	EVE	1.0	C <sub>6</sub> H <sub>6</sub>		23 $\pm$ 3
Ph <sub>2</sub> CO	0.2	EVE	1.3	CH <sub>3</sub> CN <sup>c</sup>		27 $\pm$ 3
Ph <sub>2</sub> CO	0.2	EVE	1.3	<i>t</i> -BuOH		23 $\pm$ 3
Ph <sub>2</sub> CO	0.1	EVE	0.3	C <sub>6</sub> H <sub>6</sub>	+ <i>d</i>	22 $\pm$ 4
PhCHO	0.1	EVE	0.2	C <sub>6</sub> H <sub>6</sub>		27 $\pm$ 3
PhCHO	0.4	EVE	1.2	C <sub>6</sub> H <sub>6</sub>		30 $\pm$ 3
PhCHO	0.15	EVE	0.5	C <sub>6</sub> H <sub>6</sub>	+ <i>e</i>	26 $\pm$ 4
Me <sub>2</sub> CO	1–2	EVE	Neat			25 $\pm$ 3
Me <sub>2</sub> CO	0.1	EVE	0.3	CH <sub>3</sub> CN		25 $\pm$ 5
Me <sub>2</sub> CO	0.4	EVE	2.0	CH <sub>3</sub> CN		25 $\pm$ 3
Me <sub>2</sub> CO	0.1	BVE <sup>b</sup>	0.3	CH <sub>3</sub> CN		25 $\pm$ 2
Me <sub>2</sub> CO	0.2	BVE	0.4	<i>t</i> -BuOH		31 $\pm$ 2

<sup>a</sup> Ethyl vinyl ether. <sup>b</sup> Butyl vinyl ether. <sup>c</sup> CH<sub>3</sub>CN: C<sub>6</sub>H<sub>6</sub> = 3:2. <sup>d</sup> Piperylene, *c* 0.2 mol/l. <sup>e</sup> Piperylene, *c* 0.35 mol/l.

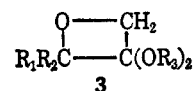
of piperylene resulted in a remarkable decrease in the rate of cycloaddition, but had no effect on the isomer ratios (Table II). These results suggest that the additions occur *via* one excited quenchable state, most likely the  $n-\pi^*$  triplet state, of the carbonyl compounds.<sup>13</sup>

Since 2- and 3-alkoxyoxetanes are virtually new types of compounds,<sup>14-16</sup> some of the isomers were separated for further characterization. 3-Alkoxyoxetanes show a characteristic infrared absorption around 980  $\text{cm}^{-1}$ , already observed for other oxetanes.<sup>9</sup> In the 2-alkoxy isomers, this band was shifted toward longer wavelengths to 940-950  $\text{cm}^{-1}$ . The nmr spectra of the isomers showed the characteristic differences in the shifts of the ring protons mentioned above. In addition, the signals corresponding to the protons in the alkoxy side chains were uniquely different in the isomers. In the 2-ethoxyoxetanes (1), the  $\alpha$ -methylene protons ( $\text{OCH}_2\text{CH}_2$ ) were nonequivalent and gave rise to complex splitting patterns (ABX<sub>3</sub> type) similar to other acetals, whereas these protons appeared as regular quartets in the 3-ethoxyoxetanes.

Separation of the 2 and 3 isomers was generally achieved by spinning-band distillation; isolation of pure 2-alkoxy isomers usually required refractionation of enriched samples. In cases where this seemed desirable, a quantitative isolation of the 3-alkoxyoxetanes from the reaction mixtures was readily achieved through the selective transformations of the 2-alkoxyoxetanes outlined in Scheme III. By proper choice of the reagents, the boiling points of the reaction products from the 2-alkoxy isomers could be selected in such a fashion that their separation from the unreacted 3-alkoxyoxetanes became quantitative. It was thus possible to study the composition of the isomeric 3-alkoxyoxetanes obtained from the cycloaddition of benzaldehyde to ethyl vinyl ether. The results showed that a 1:1 mixture of stereoisomers was formed (see Experimental Section). It is worth noting that in the oxetanes studied so far, the *cis*- and *trans*-geminal coupling constants were only slightly different. Similar effects have previously been observed in the cyclobutane series.<sup>17</sup> The isomer composition of the 2-phenyl-3-ethoxyoxetanes was confirmed by the results of their acid-catalyzed hydrolysis which led to a 1:1 mixture of diastereoisomeric 1-phenyl-3-ethoxypropane-1,3-diols.<sup>12</sup>

**Ketene Acetals.**— $\alpha,\beta$ -Unsaturated ketones have been found to react with ketene acetals under irradiation to give dialkoxycyclobutanes as the major<sup>18,19</sup> or the only<sup>19,20</sup> products, 3,3-dialkoxyoxetanes being side products in some cases.<sup>18,19</sup> Our results obtained from the cycloaddition of saturated carbonyl compounds to

vinyl ethers prompted an extension of the studies to ketene acetals. Acetone, cyclohexanone, propionaldehyde, benzaldehyde and benzophenone all added readily to ketene diethyl acetal. Pure 3,3-dialkoxyoxetanes (3) could be isolated from the reaction mixtures by distillation and/or crystallization. The



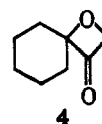
nmr and infrared spectra of these compounds showed the same characteristic absorption bands observed for the 3-alkoxyoxetanes. Further analogy between the 3-alkoxy and 3,3-dialkoxy compounds was found in the patterns of their respective mass spectra. These did not show molecular ion peaks, but fragments derived from the loss of formaldehyde from the oxetane (Table III).

TABLE III  
MASS SPECTRAL DATA FOR 3-ALKOXY-  
AND 3,3-DIALKOXYOXETANES

$\begin{array}{c} \text{O} - \text{CHR}_5 \\   \quad   \\ \text{R}_1\text{R}_2\text{C} - \text{CR}_3\text{R}_4 \end{array}$		Mol wt	Highest mass fragment			
R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>		
CH <sub>3</sub>	CH <sub>3</sub>	H	OC <sub>2</sub> H <sub>5</sub>	H	130	100 <sup>a</sup>
CH <sub>3</sub>	CH <sub>3</sub>	OC <sub>2</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	H	174	144 <sup>a</sup>
CH <sub>3</sub>	CH <sub>3</sub>	OC <sub>2</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	188	144 <sup>b</sup> 130 <sup>c</sup>
C <sub>2</sub> H <sub>5</sub>	H	H	OC <sub>2</sub> H <sub>5</sub>	H	132	102 <sup>a</sup>
C <sub>2</sub> H <sub>5</sub>	H	OC <sub>2</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	H	174	144 <sup>a</sup>
(CH <sub>3</sub> ) <sub>2</sub>		H	OC <sub>2</sub> H <sub>5</sub>	H	170	140 <sup>a</sup>
(CH <sub>3</sub> ) <sub>2</sub>		OC <sub>2</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	H	214	184 <sup>a</sup>
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	H	298	268 <sup>a</sup>

<sup>a</sup> M<sup>+</sup> - CH<sub>2</sub>O. <sup>b</sup> M<sup>+</sup> - CH<sub>3</sub>CHO. <sup>c</sup> M<sup>+</sup> - (CH<sub>3</sub>)<sub>2</sub>CO.

Hydrolysis of the cyclohexanone-ketene diethyl acetal adduct gave a moderate yield of 1-oxaspiro[3.5]nonan-3-one (4) which had data in good agreement



with those previously reported.<sup>21</sup> The structural assignment was further supported by the ir spectrum of the ketone which showed a carbonyl absorption at 1815  $\text{cm}^{-1}$ , characteristic<sup>22</sup> for 3-oxetanones, as well as by its nmr spectrum which consisted of a singlet at  $\tau$  4.93 and a multiplet at *ca.*  $\tau$  8.3.

2,2-Dialkoxyoxetanes have not yet been reported in the literature. The nmr spectra of the reaction mixtures from the irradiation of acetone and cyclohexanone with ketene diethyl acetal showed singlets at  $\tau$  7.64 and 7.76, respectively, signals expected for 2,2-dialkoxyoxetanes. Distillation of these mixtures afforded fractions enriched in the 2,2-dialkoxy isomers, but isolation in a high state of purity could not be achieved. The oxetanes were therefore characterized

(13) NOTE ADDED IN PROOF.—It has meanwhile been shown in a study of the photocycloaddition of acetone to methyl  $\beta$ -ethylvinyl ether that such additions may occur both through the singlet and/or the triplet state, depending on experimental conditions [N. J. Turro and P. Wriede, *J. Amer. Chem. Soc.*, **90**, 6863, (1968)]. Addition of quenchers in this system also did not effect the ratio of 2- to 3-alkoxyoxetanes; i.e., both excited states lead to the same ratio of 2 to 3 isomers.

(14) The preparation of some 2- and 3-alkoxyoxetanes by nonphotochemical routes has recently been reported; cf. ref 15 and 16.

(15) (a) F. Nerdel, D. Frank, H.-J. Lengert, and P. Weyerstahl, *Chem. Ber.*, **101**, 1850 (1968); (b) J. Jančulev, F. Nerdel, D. Frank, and G. Barth, *ibid.*, **100**, 715 (1967); (c) F. Nerdel and H. Kressin, *Ann.*, **707**, 706 (1967).

(16) N. P. Gambaryan, L. A. Simonyan, and P. V. Petrovskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 918 (1967). R. J. Polak, J. A. Wojtowicz, and J. A. Zaslowsky, Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, p Q43.

(17) R. Steinmetz, W. Hartmann, and G. O. Schenck, *Chem. Ber.*, **98**, 3854 (1965), and references cited therein.

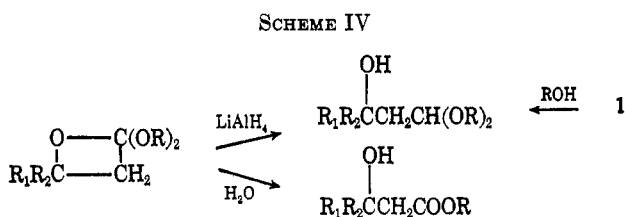
(18) O. L. Chapman, T. H. Koch, F. Klein, P. J. Nelson, and E. L. Brown, *J. Amer. Chem. Soc.*, **90**, 1657 (1968).

(19) (a) N. C. Yang, *Pure Appl. Chem.*, **9**, 591 (1964); (b) J. W. Hanifin and E. Cohen, *Tetrahedron Lett.*, 5421 (1966).

(20) E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *J. Amer. Chem. Soc.*, **86**, 5570 (1964).

(21) J. R. Marshall and J. Walker, *J. Chem. Soc.*, 467 (1952).

(22) (a) S. Searles, Jr., in "Heterocyclic Compounds," Vol. II/2, A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1964, p 983; (b) G. Dittus in Houben Weyl's "Methoden der organischen Chemie," Vol. VI/3, Georg Thieme Verlag, Stuttgart, 1963, p 515.



via their transformation products (Scheme IV). In general, a similar difference in reactivity was observed between 2,2- and 3,3-dialkoxy isomers as was found between 2- and 3-dialkoxyoxetanes. Treatment of the mixtures of the isomeric oxetanes with excess lithium aluminum hydride in refluxing diethyl ether resulted in complete, selective conversion of the 2,2 isomers into the corresponding 3-hydroxy acetals. These acetals were readily separated from the unreacted 3,3-dialkoxyoxetanes by preparative vpc. They were identified by comparison with the compounds independently prepared by alcoholysis of the corresponding 2-alkoxyoxetanes.<sup>12</sup> Likewise, mixtures of 2,2- and 3,3-dialkoxyoxetanes, when treated with water, gave mixtures of unreacted 3,3-dialkoxy isomers and 3-hydroxy esters (for details, see Experimental Section). The presence of 2,2-dialkoxyoxetanes in the irradiation mixtures from acetone and cyclohexanone was thus unequivocally established.

Irradiation of benzophenone with ketene diethyl acetal also leads to a considerable amount of the 2,2-dialkoxyoxetane. This was demonstrated by isolating 3,3-diphenyl-3-hydroxypropionaldehyde diethyl acetal after  $\text{LiAlH}_4$  reduction of the irradiation mixtures. Despite several attempts, no 2,2-dialkoxyoxetanes could be detected in the irradiation mixtures from benzaldehyde and propionaldehyde with ketene diethyl acetal. In these irradiations, the disappearance of the acetal and the carbonyl compounds were much faster than in other cases. Further, the reaction mixtures contained very large amounts of high molecular weight materials, even after short irradiation times. It seems likely, therefore, that in analogy to all the other cases, 2,2-dialkoxyoxetanes are also formed with these aldehydes, but that they are destroyed subsequently. The results from the addition to ketene diethyl acetal are summarized in Table IV.

### Discussion

**Products.**—A striking feature in the photocycloaddition to the vinyl ethers is the good yields obtained with aliphatic and alicyclic ketones. Whereas oxetanes are usually quite readily available from the reaction of aromatic ketones with olefins,<sup>23</sup> the addition of aliphatic ketones generally does not represent a useful synthetic method.<sup>10,22-24</sup> Because of the high energy levels of the excited states of such aldehydes and ketones, hydrogen abstraction and/or energy transfer (leading to dimerization of the olefin) often compete with oxetane formation.<sup>9</sup> Oxetanes are useful interme-

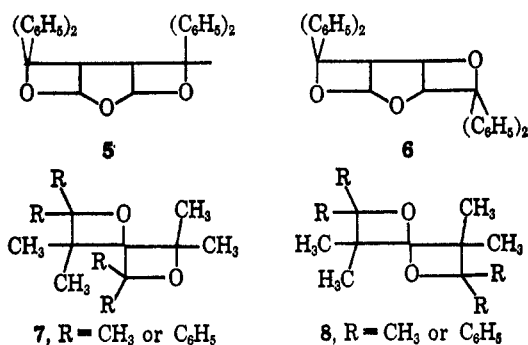
TABLE IV  
PRODUCT COMPOSITION OF DIALKOXYOXETANES FROM THE  
PHOTOCHEMICAL CYCLOADDITION OF CARBONYL COMPOUNDS  
TO KETENE DIETHYL ACETAL

Carbonyl compound	Solvent	2,2-Dialkoxy-oxetane, <sup>a</sup> %	Method of identification <sup>b</sup>
Acetone	Acetone	30 ± 5	Nmr, hydrolysis, $\text{LiAlH}_4$ reduction
Cyclohexanone	Cyclohexanone	30 ± 5	Nmr, hydrolysis, $\text{LiAlH}_4$ reduction
	<i>t</i> -BuOH <sup>c</sup>	30 ± 5	Nmr
	$\text{CH}_3\text{CN}^c$	30 ± 5	Nmr
Benzophenone	Benzene	21 ± 5	$\text{LiAlH}_4$ reduction
Propionaldehyde	Pentane	None	$\text{LiAlH}_4$ reduction
Benzaldehyde	Benzene	None	$\text{LiAlH}_4$ reduction

<sup>a</sup> 2,2-Dialkoxy + 3,3-dialkoxyoxetane = 100%. <sup>b</sup> Identification of the 2,2-dialkoxyoxetane. <sup>c</sup> [Cyclohexanone] = 0.1 mol/l.; [ketene diethyl acetal] = 0.4 mol/l.

diates; they react with a large variety of reagents under ring opening to give 3-substituted hydroxy compounds or derivatives thereof.<sup>22</sup> So far, these reactions have been of theoretical rather than of practical interest, since oxetanes have generally been prepared by ring closure of such difunctional compounds.<sup>22</sup>

**Mechanism.**—Cycloadditions to vinyl ether systems have recently been reported in a few special cases. In the second addition of carbonyl compounds to allenes<sup>5</sup> or furans,<sup>6</sup> the unsaturated system is a vinyl ether. The mode of addition of carbonyl compounds to the systems studied in this paper is not predictable from these results, however. In the case of the second addition of benzophenone to furan, more of the 2-alkoxy isomer **5** (as compared with **6**) was formed,<sup>6b,d</sup> whereas addition of benzophenone and acetone to tetramethylallene<sup>5</sup> has been reported<sup>5a</sup> to give more of the 3-alkoxy isomer **7** than of the 2 isomer **8**. It has



been pointed out<sup>5b</sup> that, in the latter reactions, methyleneoxetanes might not be representative examples of acyclic vinyl ethers.

The isomer ratios given in Tables I, II, and IV show that the addition of the carbonyl compounds to both vinyl ethers and ketene acetals occurs preferentially, though by no means exclusively, in an anti-Markovnikov fashion with regard to ground-state polarizations. Anti-Markovnikov addition would be predicted by the biradical mechanism discussed above since the stabilizing effect of alkoxy substituents is well known from the radical addition reactions to vinyl

(23) L. L. Muller and J. Hamer in "1,2-Cycloaddition Reactions," Interscience Publishers, New York, N. Y., 1967, Chapter III.

(24) (a) J. S. Bradshaw, *J. Org. Chem.*, **31**, 237 (1966); (b) P. DeMayo, J. B. Stothers, and W. Templeton, *Can. J. Chem.*, **39**, 488 (1961).

ethers and ketene acetals.<sup>25,26</sup> However, the formation of a large proportion of 2-alkoxyoxetanes in the photoadditions to vinyl ethers indicates that factors other than the stability of the intermediate biradicals must play an important role in determining the mode of photocycloaddition. Otherwise, one would expect similar orientational specificity in the photocycloaddition reaction in comparison to the free radical additions where anti-Markovnikov additions are exclusively observed.<sup>25,26</sup>

Even more surprising is the fact that relatively large proportions of 2,2-alkoxyoxetanes are found in the photoadditions to ketene acetals. If radical stability of the intermediates were the only determining factor in the cycloaddition reaction, one would expect the isomer ratio to change considerably in changing from vinyl ethers to ketene acetals—which is not the case.

At this time, we can only speculate on the various factors that determine the addition. One might expect that the rate of formation of the intermediates may depend on electronic as well as on steric factors. The actual polarization of the carbonyl group in the excited state (as yet unknown) will certainly play an important role in the addition to such highly polarized molecules as vinyl ethers or ketene acetals. The formation of the intermediate may be reversible<sup>27</sup> owing to a second energy barrier separating intermediates and products (Figure 1). Further work designed to understand more fully the mechanism, of these photo-reactions is currently in progress in this laboratory.

### Experimental Section

Ethyl vinyl, *n*-butyl vinyl and isobutyl vinyl ether were obtained from commercial sources, dried, and fractionated over sodium. Acetone was dried over calcium chloride and fractionated over potassium permanganate. Irradiations were carried out under nitrogen in internally water-cooled reactors at 15–25° with a 450-W medium-pressure mercury lamp. For reactions with aliphatic ketones and aldehydes, a quartz reactor was used in combination with a Vycor 7910 glass filter to eliminate wavelengths below 2500 Å. Irradiations with aromatic aldehydes, aryl alkyl ketones and diaryl ketones were carried out in Pyrex vessels. Care was taken to protect the reaction mixtures from moisture since 2-alkoxyoxetanes and ketene acetals react with water at room temperature. Most gas chromatographic analyses were carried out on a 3-ft Apiezon L column on a dual column, temperature-programmed 5750 F & M research chromatograph. 2-Alkoxyoxetanes were found to be unstable on virtually all other columns. Nmr spectra were recorded on a Varian A-60 and ir spectra on a Perkin-Elmer Model 337 spectrometer. Coupling constants are approximate values ( $\pm 1$  cps). Elemental analyses and molecular weight determinations were obtained from Galbraith and Schwarzkopf Microanalytical Laboratories. The substituted alkoxy and dialkoxyoxetanes are consistently named in such a fashion that they appear either as 2- or 3-alkoxyoxetanes (or 2,2- and 3,3-dialkoxyoxetanes, respectively).

**Acetone-Ethyl Vinyl Ether.**—A solution of 43.5 g (0.75 mol) of acetone in 300 ml of ethyl vinyl ether was irradiated for 50 hr. Excess ethyl vinyl ether was carefully removed at 50 mm and the residue distilled to afford 59 g (60.5%) of a mixture of alkoxyoxetanes, bp 60–80° (70 mm). Vpc analysis on a 2-ft

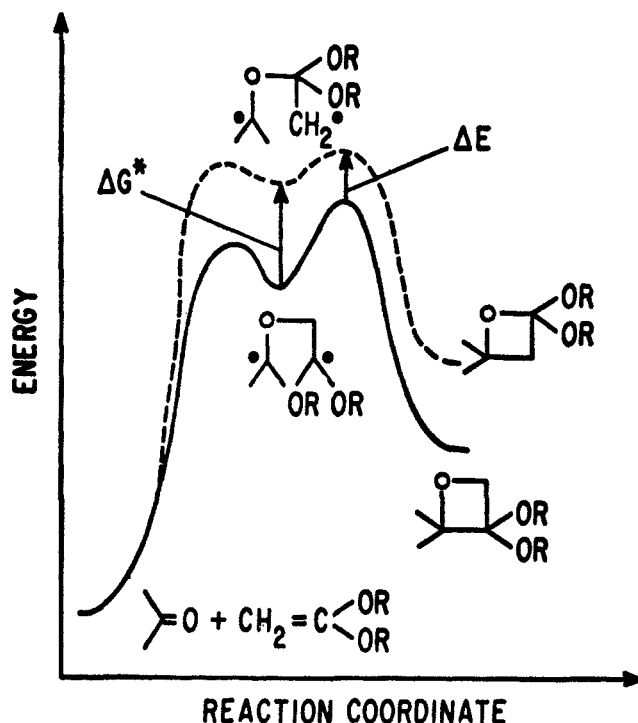


Figure 1.

Apiezon column showed this to be a 25:75 mixture of isomers. Comparison of the nmr signals at  $\tau$  4.8, 5.8 and 7.8 gave a 30:70 ratio of 4,4-dimethyl-2-ethoxy- to 2,2-dimethyl-3-ethoxyoxetane. Distillation through an 80-cm spinning-band column afforded 35 g of 2,2-dimethyl-3-ethoxyoxetane, bp 67–68° (65 mm),  $n_D^{20}$  1.4103, which was shown to be free from its isomer by nmr and vpc analysis: ir (neat,  $\text{cm}^{-1}$ ) 890 vs, 960 vs; nmr (neat)  $\tau$  5.50–6.12 (m, 3, eight-line spectrum), 6.62 (q, 2), 8.69 (s) and 8.87 (t) of 9-H.

*Anal.* Calcd for  $\text{C}_7\text{H}_{14}\text{O}_2$ : C, 64.58; H, 10.84; mol wt, 130.18. Found: C, 64.58; H, 10.85; mol wt, 174.

**4,4-Dimethyl-2-ethoxyoxetane** [bp 54° (62 mm),  $n_D^{20}$  1.4002] was obtained by careful fractionation of enriched samples. It was shown to be free of its 3 isomer by vpc and nmr analysis: ir ( $\text{CCl}_4$ ,  $\text{cm}^{-1}$ ) 980 w, 940 vs; nmr (neat)  $\tau$  4.69 (s), 4.76 (s), 4.78 (s) and 4.75 (s) of 2-H, ca. 6.5 (14-line spectrum, 2-H), 7.33–7.99 (eight-line spectrum, 2-H), 8.61 (s), 8.64 (s) and 8.83 (t) of 9-H.

*Anal.* Calcd for  $\text{C}_7\text{H}_{14}\text{O}_2$ : C, 64.58; H, 10.84. Found: C, 64.74; H, 10.74.

**Acetone-*n*-Butyl Vinyl Ether.**—A solution of 100 g of *n*-butyl vinyl ether in 200 ml of acetone was irradiated for 22 hr. Distillation gave 156 g of an azeotropic mixture of acetone and *n*-butyl vinyl ether, bp 55–95°, containing 24 g of the vinyl ether (via vpc), 8 g of *n*-butyl vinyl ether [bp 65° (95 mm)], and 60 g (60%) of a 75:25 mixture (via vpc and nmr) of 2,2-dimethyl-3-*n*-butoxy- and 4,4-dimethyl-2-*n*-butoxyoxetane. This mixture was fractionated through an 80-cm spinning-band column to afford 21.2 g of pure (>99% by vpc) 2,2-dimethyl-3-*n*-butoxyoxetane: bp 70° (16 mm);  $n_D^{20}$  1.4200; ir (neat,  $\text{cm}^{-1}$ ) 980 vs, 960 vs; nmr (neat)  $\tau$  5.5–6.12 (m, 3, ABC spectrum), 6.69 (m, 2), 8.3–8.7 (m, 11) with 8.68 (s), 9.08 (m, 3).

*Anal.* Calcd for  $\text{C}_9\text{H}_{18}\text{O}_2$ : C, 68.31; H, 11.47; mol wt, 158.23. Found: C, 68.12; H, 11.55; mol wt, 175.

**4,4-Dimethyl-2-*n*-butoxyoxetane** [bp 66° (18 mm),  $n_D^{20}$  1.4125] was obtained by careful fractionation of enriched samples. It was shown to contain less than 3% of its isomer by vpc analysis: ir (neat,  $\text{cm}^{-1}$ ) no OH or C=O absorption, 990 vw, 940 vs, 845 vs; nmr (neat)  $\tau$  4.72, 4.77, 4.81, 4.86 (singlets, 1, X part of ABX), 6.15–6.92 (m, 2), 7.34–7.93 (eight lines, 2, AB part), ca. 8.5 (m, 10) with 8.61 (s) and 8.65 (s), ca. 9.0 (m, 3) with 9.08 (s).

*Anal.* Calcd for  $\text{C}_9\text{H}_{18}\text{O}_2$ : C, 68.31; H, 11.47; mol wt, 158.23. Found: C, 68.49; H, 11.49; mol wt, 161.

**Acetone-Isobutyl Vinyl Ether.**—A solution of 69 g isobutyl vinyl ether in 250 ml of acetone was irradiated for 20 hr. Work-up from two such irradiations gave unreacted acetone and vinyl

(25) (a) E. S. Huyser and L. Kim, *J. Org. Chem.*, **33**, 94 (1968); (b) C. Walling and E. S. Huyser, *Org. Reactions*, **13**, 91 (1963); (c) F. W. Stacey and J. F. Harris, *ibid.*, **13**, 150 (1963); (d) A. N. Nesmeyanov, R. Kh. Freidlina, and L. I. Zakharkin, *Dokl. Akad. Nauk SSSR*, **97**, 91 (1954); *cf. Chem. Abstr.*, **49**, 8793 (1955); (e) A. V. Bogdanova and M. F. Shostakovskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 224 (1957); *Chem. Abstr.*, **51**, 10361 (1957).

(26) E. S. Huyser, R. M. Kellogg, and D. T. Wang, *J. Org. Chem.*, **30**, 4377 (1965).

(27) N. C. Yang, J. I. Cohen, and A. Shani, *J. Amer. Chem. Soc.*, **90**, 3266 (1968).

ether and 100 g (46%) of a 75:25 mixture of the 3- and 2-isobutyroxyoxetane (via nmr), 19.8 g of a fraction [bp 60–100° (0.1 mm)] and 13.9 g of residue. Fractionation of the isomer mixture afforded 44.2 g of isomer-free (via vpc and nmr) 2,2-dimethyl-3-isobutyroxyoxetane: bp 65° (17 mm);  $n_D^{20}$  1.4163; ir (neat,  $\text{cm}^{-1}$ ) 980 vs, 963 vs; nmr (neat)  $\tau$  5.48–6.12 (m, 3), 6.92 (d, 2), 7.88–8.53 (m, 1), 8.68 (s, 6) and 9.07 (d, 6).

*Anal.* Calcd for  $\text{C}_9\text{H}_{18}\text{O}_2$ : C, 68.31; H, 11.47; mol wt, 158.23. Found: C, 68.5; H, 11.6; mol wt, 165.

The enriched 2-isobutoxy isomer was converted into  $\beta$ -methyl- $\beta$ -hydroxybutyraldehyde diisobutyl acetal. A 45:55 mixture (30.0 g) of the 2- and 3-alkoxyoxetanes was refluxed in dry isobutyl alcohol for 16 hr and the product was fractionated to afford 18.62 g (97%) of the acetal: bp 60° (0.05 mm);  $n_D^{20}$  1.4274; purity 99% by vpc; ir ( $\text{CCl}_4$ ,  $\text{cm}^{-1}$ ) 3530 vs, 1120 vs, 1042 vs; nmr (neat)  $\tau$  5.27 (t, 1), ca. 5.5 (m, 5), 8.22 (d, superimposed on m) and 8.81 (s) with total of 6-H, 9.02 (s) and 9.12 (s), total of 12-H.

*Anal.* Calcd for  $\text{C}_{13}\text{H}_{26}\text{O}_3$ : C, 67.19; H, 12.15; mol wt, 232.35. Found: C, 67.27; H, 11.93; mol wt, 230.

**Propionaldehyde-Ethyl Vinyl Ether.**—A solution of 60 g of freshly distilled propionaldehyde in 250 ml of ethyl vinyl ether was irradiated for 26 hr. Evaporation of excess vinyl ether *in vacuo* and distillation afforded 65 g (49%) of a 19:81 mixture (via nmr) of 2- and 3-alkoxyoxetanes. Vpc analysis showed two peaks in a ratio of 16:84. The oxetane mixture (60 g) was refluxed with absolute ethanol for 10 hr. Vpc analysis now showed 81% of oxetanes (one peak) and 19% of a compound of higher retention time. Spinning-band distillation gave 43 g of 2-ethyl-3-ethoxyoxetanes (mixture of *cis* and *trans*): bp 63–65° (28 mm);  $n_D^{20}$  1.4173; ir ( $\text{CCl}_4$ ,  $\text{cm}^{-1}$ ) 970 vs; nmr (neat)  $\tau$  5.25–6.15 (m, 4), 6.62 (q, 2), 8.48 (m, 2), 8.88 (t, 3) and 9.13 (t, split further, 3).

*Anal.* Calcd for  $\text{C}_7\text{H}_{14}\text{O}_2$ : C, 64.58; H, 10.84; mol wt, 130.18. Found: C, 64.61; H, 10.98; mol wt, 132.

The second fraction consisted of pure (98% by vpc)  $\beta$ -hydroxy-*n*-valeraldehyde diethyl acetal: bp 42° (0.05 mm);  $n_D^{20}$  1.4242 [lit.<sup>28</sup> bp 88–90 (8–9 mm),  $n_D^{20}$  1.4262]; ir ( $\text{CCl}_4$ ,  $\text{cm}^{-1}$ ) 3630 w, 3503 vs, 1125 vs, 1065 vs; nmr (neat)  $\tau$  5.28 (t, 1), 6.1–6.7 (m, 6) and 8.1–9.1 (m, 13) with 8.83 (t).

*Anal.* Calcd for  $\text{C}_9\text{H}_{20}\text{O}_3$ : C, 61.33; H, 11.44; mol wt, 176.25. Found: C, 61.12; H, 11.41; mol wt, 180.

**Cyclohexanone-Ethyl Vinyl Ether.**—A solution of 100 g of cyclohexanone in 200 ml of ethyl vinyl ether was irradiated for 22 hr. Work-up gave 43 g of unreacted cyclohexanone, 51 g (50% based on consumed ketone) of a mixture of oxetanes and 62 g of polymeric residue. As judged by the relative intensities of the signals at  $\tau$  4.8 and 5.8, the mixture consisted of a 30:70 ratio of the 2- and the 3-ethoxy isomer. Vpc analysis also gave a 30:70 ratio. Spinning-band distillation afforded 31.5 g of pure (>99% by vpc) 3-ethoxy-1-oxaspiro[3.5]nonane: bp 72° (3.8 mm);  $n_D^{20}$  1.4555; ir (neat,  $\text{cm}^{-1}$ ) 975 vs, 940 vs, 925 m, 910 vs; nmr (neat)  $\tau$  5.49–6.20 (nine lines, 3, ABC spectrum), 6.70 (q, 2), 8.0–8.8 (m, 13), maxima at 8.47 and 8.88.

*Anal.* Calcd for  $\text{C}_{10}\text{H}_{18}\text{O}_2$ : C, 70.54; H, 10.66; mol wt, 170.24. Found: C, 70.58; H, 10.57; mol wt, 174.

**2-Ethoxy-1-oxaspiro[3.5]nonane**, which contained <2% of its isomer (via vpc), bp 56.5 (2.5 mm),  $n_D^{20}$  1.4502, was obtained by fractionation of enriched samples. In contrast to its 3 isomer, it had a pleasant, acetal-like odor: ir (neat,  $\text{cm}^{-1}$ ) no OH or C=O adsorption, 950 vs, 928 vs, 908 vs; nmr (neat)  $\tau$  4.67, 4.74, 4.77, 4.83 (singlets, 1), ca. 6.47 (14 lines, 2, X part of ABX), 7.53–8.18 (eight lines, 2, AB part,) ca. 8.3 (m, 13) with 8.83 (t).

*Anal.* Calcd for  $\text{C}_{10}\text{H}_{18}\text{O}_2$ : C, 70.54; H, 10.66; mol wt, 170.24. Found: C, 70.50; H, 10.52; mol wt, 175.

**Benzaldehyde-Ethyl Vinyl Ether.**—A solution of 53 g of freshly distilled benzaldehyde in 300 ml of ethyl vinyl ether was irradiated for 30 hr until all the benzaldehyde had disappeared. Vpc analysis of the crude mixture gave no separation of isomers. Distillation afforded 75.05 g (85%) of oxetanes and 6 g of undistillable residue. Spinning-band distillation led to enrichment of the isomers. Two fractions of bp 65° (0.2 mm) (no. 1) and bp 75° (0.4 mm) (no. 2) showed different ir intensities [no. 1 ( $\text{CCl}_4$ ,  $\text{cm}^{-1}$ ) 930 vs, 980 w; no. 2, 930 w, 980 vs], but had virtually the same nmr spectrum.

*Anal.* Calcd for  $\text{C}_{11}\text{H}_{14}\text{O}_2$ : C, 74.13; H, 7.92; mol wt,

178.22. Found: (no. 1, no. 2): C, 74.03, 74.33; H, 8.05, 8.14; mol wt, 179, 180.

A distilled mixture of oxetanes (73 g) was therefore refluxed with absolute ethanol. Vpc analysis then showed 75% of oxetanes and 25% of a compound of higher retention time. Distillation of this mixture afforded 63.8 g of a 47:53 mixture of *cis*- and *trans*-2-phenyl-3-ethoxyoxetanes: bp 50° (0.05 mm); nmr (neat), isomer A,  $\tau$  2.7 (m), 4.32 (d,  $J = \sim 5$  cps), 5.5 (m), 6.74 (m), 8.93 (t), and isomer B,  $\tau$  2.7 (m), 4.43 (d,  $J = \sim 5$  cps), 5.5 (m), 7.10 (m), 9.28 (t).

*Anal.* Found: C, 74.07; H, 7.94; mol wt, 178.

The second fraction consisted of 17.8 g (97%) of  $\beta$ -phenyl- $\beta$ -hydroxypropionaldehyde diethyl acetal: bp 86° (0.04 mm);  $n_D^{20}$  1.4934; ir ( $\text{CCl}_4$ ,  $\text{cm}^{-1}$ ) 3615 m, 3510 vs, 3030 m, 1600 w, 1495 s, 695 vs (phenyl), 1120 vs, 1060 vs; nmr ( $\text{CCl}_4$ )  $\tau$  2.78 (s, 5), ca. 5.4 (m, 2), ca. 6.5 (m, 5), ca. 8.2 (m, 2) and 8.88 (t, 6). *Anal.* Calcd for  $\text{C}_{13}\text{H}_{20}\text{O}_3$ : C, 69.91; H, 8.99; mol wt, 224.29. Found: C, 69.79; H, 9.10; mol wt, 226.

**Benzophenone-Ethyl Vinyl Ether.**—A solution of 20 g of benzophenone in 300 ml of ethyl vinyl ether was irradiated for 48 hr. Evaporation of excess ether and distillation afforded 26.0 g (99%) of a mixture of oxetanes, bp ca. 110° (0.1 mm), that was heated in 125 ml of absolute ethanol for 12 hr. Vpc analysis of the heated mixture showed two major components in a ratio of 73:23. These were separated by spinning-band distillation. 2,2-Diphenyl-3-ethoxyoxetane had bp 118° (0.25 mm); ir ( $\text{CCl}_4$ ,  $\text{cm}^{-1}$ ) 1600 w, 1495 s, 1450 s, 1175 and 1130 vs, 980 vs, 695 vs; nmr ( $\text{CCl}_4$ )  $\tau$  2.8 (m, 10), ca. 5.4 (m, 3), 6.75 (q, 2) and 9.12 (t, 3).

*Anal.* Calcd for  $\text{C}_{17}\text{H}_{18}\text{O}_2$ : C, 80.28; H, 7.13; mol wt, 254.31. Found: C, 80.25; H, 7.36; mol wt, 242.

The second fraction consisted of  $\beta, \beta$ -diphenyl- $\beta$ -hydroxypropionaldehyde diethyl acetal: bp 133° (0.3 mm); ir ( $\text{CCl}_4$ ,  $\text{cm}^{-1}$ ) 3480 vs, 1600 w, 1495 s, 1450 s, 1175 s, 1120 vs, 1060 vs, 700 vs; nmr ( $\text{CCl}_4$ )  $\tau$  2.5–2.9 (m, 10), 5.25 (s, 1, OH), 5.57 (t, 1, CH(OR)<sub>2</sub>), 5.59 (m, 4), 7.56 (d, 2,  $J = 6$  cps), 8.94 (t, 6).

*Anal.* Calcd for  $\text{C}_{19}\text{H}_{24}\text{O}_3$ : C, 75.97; H, 8.05; mol wt, 300.38. Found: C, 75.84; H, 7.93; mol wt, 299.

**Acetone-Ketene Diethyl Acetal.**—A solution of 59 g of ketene diethyl acetal<sup>29</sup> in 300 ml of dry acetone was irradiated for 22 hr. Excess acetone was evaporated *in vacuo* and the residue was distilled to give a major fraction (43.6 g) of bp 60–90° (14 mm), one (3.8 g) of bp 65–100° (0.3 mm) and 1.8 g of a polymeric residue. The major fraction was shown to be a 73:27 mixture of 2,2-dimethyl-3,3-diethoxy- and 4,4-dimethyl-2,2-diethoxyoxetane by measuring the relative intensities of the nmr signals at  $\tau$  5.78 (s) and 7.64 (s). Fractionation of the major fraction through an 80-cm spinning-band column gave 20.1 g (23%) of the pure 2,2-dimethyl-3,3-diethoxyoxetane: bp 85–86° (12 mm); ir (neat,  $\text{cm}^{-1}$ ) 1195, 1177, 1068, 1050, 985 (all vs), 960 s, 943 s, no carbonyl absorption; nmr (neat)  $\tau$  5.78 (s, 1), ca. 6.6 (m, 2), 8.68 (s) and 8.83 (t) of 6-H.

*Anal.* Calcd for  $\text{C}_9\text{H}_{18}\text{O}_3$ : C, 62.04; H, 10.41; mol wt, 174.23. Found: C, 62.05; H, 10.51; mol wt, 180.

In another preparation, irradiation was carried out with a Corex filter until half of the ketene acetal had been consumed and the mixture of oxetanes was distilled at 40–60° (6 mm), bath temperature  $\leq 80^\circ$ . This fraction (B) showed 30  $\pm$  5% 2 isomer by nmr analysis.

**Hydrolysis of 4,4-Dimethyl-2,2-diethoxyoxetane.**—A mixture consisting of both isomeric dimethyldialkoxyoxetanes (fraction B) was dissolved in acetone and water was added until the solution became cloudy. This mixture was allowed to stand at room temperature for 10 hr. Vpc analysis now showed unreacted 2,2-dimethyl-3,3-diethoxyoxetane (75.5%) together with ethyl 3-methyl-3-hydroxybutyrate (24.5%). The ester was isolated by preparative vpc: ir (neat,  $\text{cm}^{-1}$ ) 3450, 1725, 1250, 1035, 910; nmr ( $\text{CCl}_4$ )  $\tau$  8.78 (s) and 8.73 (t) of 9-H, 7.6 (s, 2), 6.78 (s, 1), 5.83 (q, 2).

*Anal.* Calcd for  $\text{C}_7\text{H}_{14}\text{O}_3$ : C, 57.51; H, 9.65; mol wt, 146.18. Found: C, 57.72; H, 9.81; mol wt, 150.

**$\text{LiAlH}_4$  Reduction of 4,4-Dimethyl-2,2-diethoxyoxetane.**—An ether solution containing both isomeric dimethyldiethoxyoxetanes (fraction B) was added to excess  $\text{LiAlH}_4$  and the mixture was refluxed for 30 min. Work-up with acetone and water gave a mixture consisting of unreacted 2,2-dimethyl-3,3-diethoxyoxetane (71%) and of 3-methyl-3-hydroxybutyraldehyde diethyl

(28) L. A. Yanovskaya, V. F. Kucherov, and B. G. Kovalev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 647 (1962); *Chem. Abstr.*, 57, 16379c (1962).

(29) S. M. McElvain and D. Kundiger, "Organic Syntheses," Coll. Vol. III, John Wiley & Sons, Inc., New York, N. Y., 1955, p 501.



acetal (29%) which was identified by comparison of its spectra with those of an authentic<sup>12</sup> sample.

**Cyclohexanone-Ketene Diethyl Acetal.**—A solution of 50 g of ketene diethyl acetal<sup>29</sup> in 200 ml of freshly distilled cyclohexanone was irradiated for 19.5 hr. Excess cyclohexanone was removed at 20 mm through a spinning-band column and the residue was distilled to afford 60 g of a fraction of bp 65–105° (0.5 mm) and 16.0 g of undistillable residue. Nmr intensities of the signals at  $\tau$  5.79 (s) and 7.76 (s) showed the major fraction to consist of a 70:30 mixture of the 3- and the 2-dialkoxy isomers. Fractionation afforded 22.2 g (24%) of pure 3,3-diethoxy-1-oxaspiro[3.5]nonane: bp 85–86° (2.0 mm); ir (neat,  $\text{cm}^{-1}$ ) 1200 vs, 1068 vs, 1058 vs, 990 vs; nmr (neat)  $\tau$  5.80 (s, 2), 6.58 (q, 4), ca. 8.55 (m, 9) with 8.83 (t).

*Anal.* Calcd for  $\text{C}_{12}\text{H}_{22}\text{O}_5$ : C, 67.25; H, 10.35; mol wt, 214.30. Found: C, 67.15; H, 10.43; mol wt, 214.

**Hydrolysis of 2,2-Dialkoxy-1-oxaspiro[3.5]nonane.**—A mixture consisting of both isomeric dialkoxyoxaspiropanones was dissolved in acetone, water was added until the mixture was almost cloudy and the solution was allowed to stand at room temperature for 12 hr. Vpc analysis showed two major components that were separated by preparative vpc and identified as unreacted 3,3-diethoxy-1-oxaspiro[3.5]nonane and as ethyl 1-hydroxycyclohexylacetate: ir ( $\text{CCl}_4$ ,  $\text{cm}^{-1}$ ) 3530 vs, 1720 vs, 1175 vs; nmr (neat)  $\tau$  5.86 (q, 2), 6.53 (s, 1, OH), 7.60 (s, 2,  $\text{CH}_2$ ), 8.48 (m) and 8.79 (t) of 18-H.

*Anal.* Calcd for  $\text{C}_{10}\text{H}_{18}\text{O}_5$ : C, 64.49; H, 9.74; mol wt, 186.24. Found: C, 64.64; H, 9.85; mol wt, 190.

**$\text{LiAlH}_4$  Reduction of 2,2-Diethoxy-1-oxaspiro[3.5]nonane.**—A mixture containing both isomeric dialkoxyoxaspiropanones was dissolved in ether and added to excess  $\text{LiAlH}_4$ . The mixture was refluxed for 1 hr and decomposed with acetone and water. Vpc analysis showed two major components that were isolated by preparative vpc and identified as unreacted 3,3-diethoxy-1-oxaspiro[3.5]nonane and as 1-hydroxycyclohexyl acetaldehyde diethyl acetal: ir ( $\text{CCl}_4$ ,  $\text{cm}^{-1}$ ) 3564 vs, 1125 vs, 1050 vs; nmr (neat)  $\tau$  5.27 (t, 1), 6.45 (m) and 6.6 (s, OH) of 5-H, 8.28 (d), 8.52 (m) and 8.84 (t) of 18-H. The ir and nmr spectra were identical with those of the acetal prepared by ethanolytic of 2-ethoxy-1-oxaspiro[3.5]nonane.<sup>12</sup>

**Hydrolysis of 3,3-Diethoxy-1-oxaspiro[3.5]nonane.**—A mixture of 21 g of 3,3-diethoxy-1-oxaspiro[3.5]nonane, 500 ml of benzene, 5 ml of water and 2 g of *p*-toluenesulfonic acid monohydrate was refluxed for 4 hr. Most of the benzene was then slowly distilled off and the residual solution was extracted with sodium bicarbonate solution and brine and dried ( $\text{MgSO}_4$ ). Vpc analysis of this mixture indicated it to consist of a complex mixture, containing about 30% 1-oxaspiro[3.5]nonan-3-one which showed the lowest retention time. The products from two such preparations were combined and the mixture was distilled on a spinning-band column to afford 4.75 g (20%) of 1-oxaspiro[3.5]nonan-3-one: bp 67° (18 mm);  $n_D^{20}$  1.4642;  $\lambda_{\text{max}}$  (hexane) 290  $\mu$  ( $\log \epsilon$  1.8) [lit.<sup>21</sup> bp 86° (28 mm),  $n_D^{18}$  1.4631,  $\lambda_{\text{max}}$  (hexane) 290  $\mu$  ( $\log \epsilon$  1.4)]; ir ( $\text{CCl}_4$ ,  $\text{cm}^{-1}$ ) 1815; nmr (neat)  $\tau$  4.93 (s, 2), 8.0–8.5 (m, 11). The mass spectrum showed no molecular ion peak; the highest mass peak appeared at 112 (molecular weight – CO). The semicarbazone had mp 194° (from ethanol) [lit.<sup>21</sup> mp 194°].

*Anal.* Calcd for  $\text{C}_9\text{H}_{16}\text{O}_2$ : C, 68.54; H, 8.63; mol wt, 140.18. Found: C, 68.74; H, 8.63; mol wt, 145.

The higher boiling fractions consisted of saturated and unsaturated carbonyl compounds, as indicated by ir and nmr.

**Propionaldehyde-Ketene Diethyl Acetal.**—A solution of 30 g of freshly distilled propionaldehyde and 60 g of ketene diethyl acetal<sup>29</sup> in 250 ml of dry pentane was irradiated for 24 hr. The pentane was removed through a small Vigreux column and the residue distilled *in vacuo* to afford (a) 8.02 g of a mixture consisting of ketene acetal and ortho ester [bp 60–70° (97 mm)]; (b) 5.52 g of a fraction of bp 70–80° (97 mm); (c) 34.52 g (38.4%) of oxetane [bp 70–90° (18 mm)]; (d) 16.2 g of a fraction of bp 90–110° (18–0.1 mm); and (e) 6.5 g of undistillable residue. No 4-ethyl-2,2-diethoxyoxetane could be detected. Reduction of the crude reaction mixture with  $\text{LiAlH}_4$  did not give any 3-hydroxyvaleraldehyde diethyl acetal. Pure 2-ethyl-3,3-diethoxyoxetane of bp 74.5° (13 mm) was obtained by spinning-band distillation of fraction c: ir (neat,  $\text{cm}^{-1}$ ) 985 vs and 950 vs; nmr (neat)  $\tau$  5.57 (t) and 5.68 (s) of 3-H, 6.59 (q, 4), 8.38 (m), 8.83 (t) and 9.12 (t) of 11-H.

*Anal.* Calcd for  $\text{C}_9\text{H}_{18}\text{O}_5$ : C, 62.04; H, 10.41; mol wt, 174.23. Found: C, 62.0; H, 10.6; mol wt, 178.

**Benzaldehyde-Ketene Diethyl Acetal.**—A solution of 31.8 g (0.03 mol) of freshly distilled benzaldehyde and 38.5 g (0.03 mol) of ketene diethyl acetal<sup>29</sup> in 400 ml of dry benzene was irradiated for 20 hr. During this time, the solution turned intense yellow. Evaporation of the benzene *in vacuo* left a residue that gave (a) 15.8 g of unreacted aldehyde, (b) 17.44 g (39.5% based on consumed aldehyde) of crude oxetane, bp 110–140° (0.1 mm), and (c) 16 g of undistillable residue. No 4-phenyl-2,2-diethoxyoxetane could be detected; reduction of the crude reaction mixture with excess  $\text{LiAlH}_4$  failed to produce any 3-phenyl-3-hydroxypropionaldehyde diethyl acetal. Distillation of fraction b over a 60-cm spinning-band column afforded 2-phenyl-3,3-diethoxyoxetane: bp 85° (0.3 mm); ir (neat,  $\text{cm}^{-1}$ ) 985 vs, 950 s, weak absorption at 1715; nmr (neat)  $\tau$  2.7 (m), 4.47 (s), 5.43 (s, ?), 6.37–7.23 (m), 8.79 (t) and 9.21 (t).

*Anal.* Calcd for  $\text{C}_{13}\text{H}_{18}\text{O}_5$ : C, 70.24; H, 8.16; mol wt, 222.24. Found: C, 70.34; H, 8.19; mol wt, 213.

**Benzophenone-Ketene Diethyl Acetal.**—A solution of 15 g (82 mmol) of benzophenone and 10.4 g (90 mmol) of ketene diethyl acetal<sup>29</sup> in 220 ml of dry benzene was irradiated for 13 hr. The light yellow solution was concentrated *in vacuo* to leave 25.0 g of a yellow liquid. Vacuum distillation gave (a) 10.34 g of a colorless liquid, bp 120° (0.01 mm), which was shown to be a 40:60 mixture of benzophenone and 2,2-diphenyl-3,3-diethoxyoxetane by vpc analysis, and (b) a second fraction, 2.33 g, which solidified on standing (12.67 g = 52.1%). Fraction a gave 5.68 g of oxetane upon cooling its hexane solution. The solids from fractions a and b were shown to be identical by nmr and vpc analysis. They were combined and recrystallized from hexane to give 2,2-diphenyl-3,3-diethoxyoxetane as colorless plates: mp 68–70°; ir (KBr,  $\text{cm}^{-1}$ ) 1206, 1180, 1120, 1050, 985 (all vs); nmr ( $\text{CCl}_4$ )  $\tau$  2.68 (m, 5), 5.45 (s, 1), 6.79 (m, 2), 9.15 (t, 3).

*Anal.* Calcd for  $\text{C}_{19}\text{H}_{22}\text{O}_5$ : C, 76.48; H, 7.43; mol wt, 298.33. Found: C, 76.48; H, 7.54; mol wt, 296.

Reduction of the crude reaction mixture by  $\text{LiAlH}_4$  in refluxing ether gave a mixture consisting of unreacted 2,2-diphenyl-3,3-diethoxyoxetane (79%) and of  $\beta$ , $\beta$ -diphenyl- $\beta$ -hydroxypropionaldehyde diethyl acetal (21%) which were separated by preparative vpc. The acetal was identified by comparison with the authentic sample obtained from 4,4-diphenyl-2-ethoxyoxetane (see above) and by its analysis.

*Anal.* Calcd for  $\text{C}_{19}\text{H}_{24}\text{O}_5$ : C, 75.97; H, 8.05. Found: C, 76.27; H, 8.74.

**Registry No.**—2,2-Dimethyl-3-ethoxyoxetane, 18267-24-8; 4,4-dimethyl-2-ethoxyoxetane, 18267-25-9; 2,2-dimethyl-3-*n*-butoxyoxetane, 18267-26-0; 4,4-dimethyl-2-*n*-butoxyoxetane, 18267-27-1; 2,2-dimethyl-3-*iso*-butoxyoxetane, 18267-28-2;  $\beta$ -methyl- $\beta$ -hydroxybutyraldehyde diisobutyl acetal, 18267-29-3; 2-ethyl-3-ethoxyoxetane (*cis*), 18267-45-3; 2-ethyl-3-ethoxyoxetane (*trans*), 18267-49-7;  $\beta$ -hydroxy-*n*-valeraldehyde diethyl acetal, 18267-30-6; 3-ethoxy-1-oxaspiro[3.5]nonane, 18267-31-7; 2-ethoxy-1-oxaspiro[3.5]nonane, 18320-75-7; 2-phenyl-3-ethoxyoxetane (*cis*), 18267-46-4; 2-phenyl-3-ethoxyoxetane (*trans*), 18267-47-5;  $\beta$ -phenyl- $\beta$ -hydroxypropionaldehyde diethyl acetal, 18267-32-8; 2,2-diphenyl-3-ethoxyoxetane, 18267-33-9;  $\beta$ , $\beta$ -diphenyl- $\beta$ -hydroxypropionaldehyde diethyl acetal, 18267-34-0; 2,2-dimethyl-3,3-diethoxyoxetane, 18267-35-1; ethyl 3-methyl-3-hydroxybutyrate, 18267-36-2; 3,3-diethoxy-1-oxaspiro[3.5]nonane, 18267-37-3; ethyl 1-hydroxycyclohexylacetate, 5326-50-1; 1-hydroxycyclohexyl acetaldehyde diethyl acetal, 18267-39-5; 1-oxaspiro[3.5]non-3-one, 18267-40-8; 2-ethyl-3,3-diethoxyoxetane, 18267-41-9; 2-phenyl-3,3-diethoxyoxetane, 18267-42-0; 2,2-diphenyl-3,3-diethoxyoxetane, 18267-43-1; ketene diethyl acetal, 2678-54-8.

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