Photocycloadditions of Some Alkyl Ketones to 1,2-Dicyanoethylene, Maleic Anhydride, and 1-Methoxy-1-butene[1]

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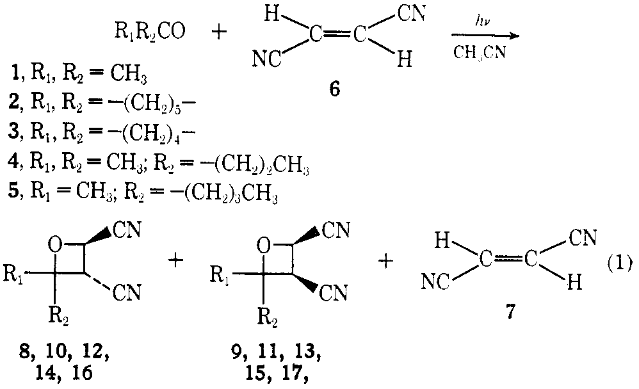
The photocycloadditions of several alkyl ketones to 1,2-dicyanoethylene, maleic anhydride, and 1-methoxy-1-butene are described. The cycloadditions are stereospecific in the case of the dicyanoethylenes but nonstereospecific in the case of 1-methoxy-1-butene. Photosensitized geometric isomerization of the ethylenes is an important side reaction. A discussion is given of the scope of these photocycloadditions and the factors which control yields and stereospecificity.

The photocycloaddition of ketones to olefins is probably the most facile method for the preparation of oxetanes. Two notable reviews by Muller and Hamer[4] and Arnold[5] have comprehensively delineated the scope of this reaction. Inspection of the available literature[4,5] indicates that oxetane formation is competitive with α cleavage,[6] hydrogen abstraction,[7] and energy-transfer[8] reactions involving the carbonyl partner and with *cis–trans* isomerization,[9] dimerization,[8] and hydrogen abstraction[10] by the excited ethylene. Excitation of the ethylene is usually accomplished by photosensitization.[11] Although the mechanism of oxetane formation is generally thought to involve attack of the S_1 or T_1 excited state of the ketone on the ethylene, several cases which appear to result from attack of the excited ethylene[12] on a ground-state carbonyl group and attack by upper excited electronic states of ketones[13] have been reported. Finally, the *reactivity* of ketones toward photocycloaddition is significantly affected by the configuration of their lowest excited singlet and triplet states; as a result the efficiency of photocycloaddition is a function both of *reactivity* and of *excited-state lifetime.*[14]

This brief outline of the factors which affect the photocycloaddition of ketones to ethylenes should be sufficient to indicate the complexities which may arise when one attempts to exploit this reaction synthetically.

We report here the synthetically useful photocycloaddition of some alkyl ketones to ethylenes.

Results



Irradiation (>2900 Å) of acetonitrile solutions of acetone (**1**) and ketones **2–5** and *trans*-1,2-dicyanoethylene (*t*-DCE) results in formation of *cis*-1,2-dicyanoethylene (*c*-DCE) and oxetanes **8–17** (eq 1). Yields of oxetane (Table I) up to 90% (based on ethylene) can be obtained on prolonged irradiation if the ethylene concentration is less than 0.5 *M*. Since the formation of oxetanes **8–17** has been shown to occur *via* a stereospecific addition of alkyl ketone singlets to DCE, while the triplet ketone causes only geometric isomerization of DCE,[15] maximum stereospecificity is obtained at high concentration of DCE, *i.e.*, conditions which favor capture of all ketone singlets before they decay to ketone triplets. An alternate method to enhance stereospecificity involves addition of a ketone triplet quencher such as 1,3-pentadiene. The latter method introduces an additional purification step and is also complicated by formation of diene dimers.[16]

TABLE I

RELATIVE QUANTUM YIELDS FOR ADDITION OF ACETONE AND KETONES 2–5 TO *t*-DEC[a,b]

Ketone	Total yield of adduct based on *t*-DCE, %
Acetone	53.7
2	70.2
3	53.0
4	40.0
5	28.7

[a] Aerated solution, 5 *M* ketone in acetonitrile; *t*-DCE, 0.5 *M*.
[b] Oxetane yields are total yields of both *cis* and *trans* adducts after 16-hr irradiation through Pyrex.

Adducts **8** and **9** have been previously characterized by Beereboom and von Wittenau.[17] The structures of adducts **10–15** are based on close correspondence of the

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(8) D. R. Arnold, R. L. Hinman, and A. H. Glick, *ibid.*, 1425 (1964).

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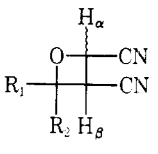
(16) G. S. Hammond, N. J. Turro, and R. S. H. Liu, *J. Org. Chem.*, **28**, 3297 (1963).

(17) J. Beereboom and M. S. von Wittenau, *ibid.*, **30**, 1231 (1965).

spectral characteristics of these compounds with those of **8** and **9**, especially the nmr (Table II) chemical shifts and couplings of protons α and β (**18**).



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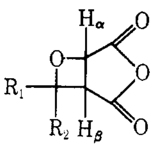

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TABLE II

CHEMICAL SHIFTS OF H_α AND H_β IN ADDUCTS 8–15[a]

Adduct	H_α	H_β	$J_{\alpha\beta}$, Hz
8	5.18	3.96	6.5
8[b]	5.65	4.53	6.5
9	5.28	4.02	8.5
9[b]	5.60	4.42	8.5
10	5.13	3.69	6.3
11	5.25	3.79	8.8
12	5.20	4.12	6.5
13	5.28	4.27	8.5
14	5.18, 5.13	3.88, 3.83	6.5
15	5.29, 5.22	4.00, 3.96	9.0

[a] Spectra taken in CCl_4; chemical shifts in parts per million from internal TMS (0.00). [b] Value of Beereboom and von Wittenau[12] in DMSO.

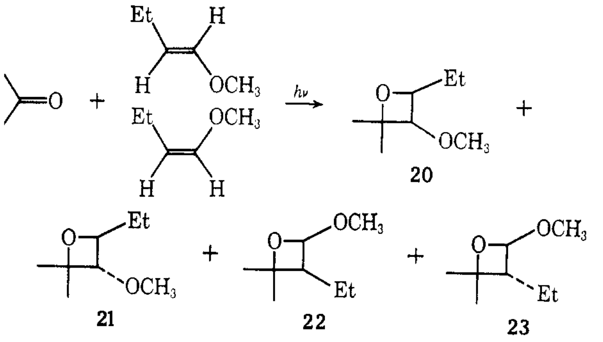
The adducts **10–15** were isolated by preparative vpc on a 6-ft 25% SE-30 column at 175°. All adducts exhibited doublets near δ 5.2 and 4.0, respectively. The former absorption is assigned to the ring hydrogen α to the ring oxygen (H_α in **18**) while the higher field absorption is assigned to the other ring hydrogen (H_β in **18**). Identification of oxetanes **10–15** is based on the excellent agreement of the chemical shifts of H_α and H_β as well as $J_{\alpha,\beta}$ in these adducts with those found for the acetone adducts **8** and **9** (Table II). Further proof for our stereochemical assignments is obtained from our observations that only the adducts with $J_{\alpha,\beta}$ = 6.5 Hz are formed in low conversion reactions of ketones **1–5** with *t*-DCE. The stereospecific nature of the addition reaction indicates that the adducts with $J_{\alpha,\beta}$ = 6.5 Hz have *trans* stereochemistry, while those with $J_{\alpha,\beta}$ = 8.5 Hz have *cis* stereochemistry.

The mass spectra of **10–15** support the oxetane structure but are not conclusive evidence for their structure. Parent ions are not observed (a not unusual situation for oxetanes[17]) and the most important fragmentation is cleavage to form DCE and a charged carbonyl fragment, the latter then undergoing further decomposition.

Photocycloaddition of ketones **1–5** occurs between these ketones and maleic anhydride. The synthetic usefulness of these reactions is limited by the competing side reactions of maleic anhydride dimerization and polymerization.[18] The adduct of acetone and maleic anhydride (**19**) was isolated by crystallization and purified by sublimation. The structure of adduct **19** was assigned mainly on the basis of its analysis and nmr spectrum, which closely resembled the spectra of the DCE adducts.

The photoaddition to *t*-DCE and maleic anhydride is apparently limited to saturated alkyl ketones. Aromatic and α,β-unsaturated ketones do not add even after prolonged irradiation, although isomerization of DCE and dimerization of maleic anhydride is observed. A possible explanation for the lack of reactivity toward photoaddition shown by aromatic ketones may be their extremely short singlet state lifetimes[19] or the more delocalized nature of the π^* electron in the case of aromatic ketone n,π^* states.

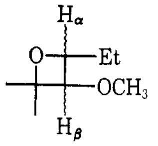
Irradiation of acetone in the presence of a mixture of *cis*- and *trans*-1-methoxy-1-butenes (MB) leads to the formation of four isomeric oxetanes, **20–23** (eq 2). Adducts **20–23** were isolated by preparative vpc on a 6-ft 20% Carbowax column at 100°. The acetal type of adduct (**22** and **23**) is very acid sensitive. Preparative vpc was therefore carried out on a gas chromatograph which had previously been conditioned by repeated injections of solutions containing sodium methoxide.



(2)

Structural identification of **20–23** is based on spectral analysis. The nmr spectra of **20** and **21** exhibit low field quartets at δ 4.40 (J = 6.5 Hz) and 4.10 (J = 5.5), respectively. These absorptions are assigned to the ring hydrogens α to the ethyl and ring oxygen (**24**). The ring protons α to the methoxyl in **20** and **21** are found at slightly higher, δ 3.87 (J = 6.5 Hz) in **20** and 3.40 (J = 5.5 Hz) in **21**.

Martin, *et al.*,[20] have prepared cyclobutanones **25** and **26** which are excellent carbocyclic analogs of oxetanes **20** and **21**. The observed nmr positions of the protons adjacent to the ethoxy group in **25** and **26** are δ 3.88 and 3.48, respectively. Furthermore, the ring hydrogen coupling constant of the *cis* ketone is 8.0 Hz, while that of the *trans* ketone is only 6.9 Hz. These results support the stereochemical assignments for **20** and **21**.



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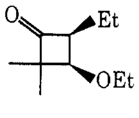

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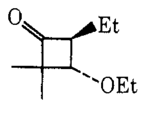

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Karplus[21] has shown that the vicinal proton coupling constants depend on the dihedral angle involved. If the oxetanes are nearly planar, then the dihedral angle for the *cis* form is 0° while the angle for the *trans* form is 127°.[20] According to the Karplus equation, the *cis* structure should exhibit the larger coupling constant.

Adducts **22** and **23** exhibited low field doublets at δ 5.00 (J = 6 Hz) and 4.70 (J = 4.0 Hz) which were assigned

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[18] W. M. Hardham and G. S. Hammond, *J. Amer. Chem. Soc.*, **89**, 3200 (1967), and references therein.

[19] W. M. Moore, G. S. Hammond, and R. P. Foss, *ibid.*, **83**, 2789 (1961).

[20] J. C. Martin, V. W. Goodlett, and R. D. Burpitt, *J. Org. Chem.*, **30**, 4309 (1965).

[21] M. Karplus, *J. Amer. Chem. Soc.*, **85**, 2870 (1963).

to the ring protons α to both the methoxy group and the ring oxygen. The other protons were observed at much higher fields (δ 2.47 and 2.15, respectively). The stereochemical assignments of **22** and **23** are based on the same arguments used for the other oxetanes.

The yield of oxetanes **20–23** approached 100% (based on olefin) after prolonged irradiation at low (~ 0.5 *M*) olefin concentrations.

Control experiments showed that the **20–24** did not equilibrate in the presence or absence of acetone. Furthermore, since at very low conversion *cis–trans* isomerization occurs to only a minor extent, the stereochemical results do not reflect loss of stereochemistry of the starting olefin, but demand stereochemical loss in some intermediate.

Discussion

The detailed mechanism of the photocycloadditions reported here will be discussed in a separate publications.[22] We shall consider here only several significant points related to the synthetic aspects of these photocycloadditions.

The absolute yields of oxetanes from DCE and alkyl ketones are good, indicating the lack of significant side reactions. Only in the case of **5** is a competitive primary photochemical process, namely type II cleavage,[23] available. The cyclic ketones **2** and **3** are known to undergo α-cleavage reactions, but this primary process occurs from the triplet,[24] so that interception of ketone singlets with high DCE concentrations makes good yields of oxetanes possible. In the case of cyclobutanone,[25] α cleavage is apparently too fast from the singlet state and no cycloaddition to DCE is observed. In the case of aryl ketones, apparently intersystem crossing is so fast that the singlet lifetimes are decreased to the extent that singlet cycloaddition is not competitive with triplet formation. In the case of α,β-unsaturated ketones, rapid twisting[26] in S_1 probably decreases singlet lifetimes to the extent that they are so short that cycloaddition *via* S_1 is insignificant. These interpretations are predicted on the assumption that T_1 is unreactive toward photocycloaddition in analogy to the case of acetone. This hypothesis seems to provide an adequate framework to rationalize the results reported here.

The important bimolecular side reactions expected of an alkyl ketone and ethylene are energy transfer and hydrogen abstraction. While the former occurs when triplet ketones interact with DCE, the S_1 state of alkyl ketones only adds to DCE but does not isomerize the ethylene. Since hydrogen abstraction is known to result from electrophilic attack by the n,π* states of alkyl ketones,[27] it is not surprising that this reaction is not significant in the case of DCE as substrate.

It is of some interest, however, that photohydrogen abstraction is not a significant reaction with MB, which has labile allylic and methoxy hydrogens. The rate constant[28] for hydrogen abstraction from isopropanol by cyclopentanone is $\sim 10^7\ M^{-1}\ \text{sec}^{-1}$. The rate constant of photocycloaddition of acetone to MB is $\sim 10^8\ M^{-1}\ \text{sec}^{-1}$. It seems that the rate constants for photocycloaddition of alkyl ketones to nonactivated alkenes probably must be generally less than $\sim 10^7\ M^{-1}\ \text{sec}^{-1}$, since hydrogen abstraction is a major competing side reaction in these cases.

Although the photocycloaddition of alkyl ketones to MB is not highly stereospecific, there is a greater degree of specificity at high MB concentrations. This result obtains because more acetone singlets are trapped at high MB concentrations.[22]

Experimental Section

General.—Nuclear magnetic resonance spectra were taken on a Varian A-60-A spectrometer using tetramethylsilane as an internal standard. Chemical shifts are reported as parts per million (TMS = 0) and coupling constants are reported as hertz. Infrared spectra were taken on a Perkin-Elmer Model 137 Infracord. Mass spectra were taken on a Hitachi Perkin-Elmer RMU-6D mass spectrometer. Gas chromatographic analyses were run on a Wilkens Aerograph A-90-P chromatograph. Elemental analyses were run by Schwarzkopf Laboratories, Woodside, N. Y., and by Micro-Tech Laboratories, Skokie, Ill.

Acetone (J. T. Baker Co., Spectroquality) was used as received. Acetonitrile (Matheson Coleman and Bell) was used as received. Cyclohexanone and cyclopentanone (Matheson Coleman and Bell) were flash distilled under vacuum before use. 2-Pentanone (Eastman Organic Chemicals) was flash distilled under vacuum before use. 2-Hexanone (J. T. Baker) was used as received. *trans*-1,2-Dicyanoethylene (Pfaltz and Bauer and Aldrich Chemical Co.) was sublimed before use. 1-Methoxy-1-butene was prepared by the method described below.

Preparation and Isolation of Adducts 10–15.—Pyrex test tubes containing acetonitrile solutions 0.5 *M* and 5.0 *M* each in *t*-DCE and ketone (cyclohexanone, cyclopentanone and 2-pentanone), respectively, were strapped to a Vycor immersion well and irradiated for 16 hr with a 450-W Hanovia medium pressure lamp at room temperature. The crude reaction mixtures (highly colored) were analyzed by nmr for extent of adduct formation. After prolonged irradiation, all solutions were found to contain nearly equal amounts of *cis*- and *trans*-DCE and roughly 3:1 ratios of *trans* to *cis* photoadducts. The total conversion of DCE to adducts was 81.5% for cyclohexanone, 64.5% for cyclopentanone, and 58.5% for 2-pentanone. The acetonitrile and excess ketone were removed under vacuum; the adducts were isolated by preparative vpc on a 6-ft 25% SE-30 column at 175°.

Adduct **10** had a retention time of 4 min at 175° and collected as a colorless oil which solidified on standing: infrared spectrum λ_{max} (CCl_4) 2924 (CH), 2252 (CN), 1449, 1002, and 910 cm^{-1} (oxetane ring); nmr δ 5.13 (d, *J* = 6.3 Hz, 1 H) ring hydrogen α to nitrile and oxygen, 3.69 (d, *J* = 6.3 Hz, 1 H) ring hydrogen α to nitrile, 2.17–1.25 (broad, 10 H) six-membered-ring methylenes. The mass spectrum of **10** did not show a parent peak; the base peak was *m/e* 98, corresponding to the loss of DCE. Other fragments were found at *m/e* (rel intensity to base peak) of 121 (3.3), 120 (5.5), 83 (16), 80 (27), 70 (35), 69 (47), 56 (20), 55 (94), 43 (21), 42 (47), 41 (43) and 39 (37).

Anal. Calcd for $C_{10}H_{12}ON_2$: C, 68.10; H, 6.81; N, 15.91. Found: C, 68.14; H, 6.87; N, 16.17.

Adduct **11** had a retention time of 9 min at 175° and collected as a viscous oil: infrared spectrum λ_{max} (CCl_4) 2222 (CN), 1018 and 985 cm^{-1} (oxetane ring); nmr δ 5.25 (d, *J* = 8.8 Hz, 1 H) ring hydrogen α to nitrile and oxygen, 3.79 (d, *J* = 8.8 Hz, 1 H) ring hydrogen α to nitrile, 2.20–1.30 (broad, 10 H) six-membered-ring methylenes.

Anal. Calcd for $C_{10}H_{12}ON_2$: C, 68.10; H, 6.81; N, 15.91. Found: C, 68.26; H, 6.74; N, 15.61.

Adduct **12** collected as a colorless, viscous oil at 175°: retention time 2.5 min; infrared spectrum λ_{max} (CCl_4) 2222 (CN), 1008 and 959 cm^{-1} (oxetane ring); nmr δ 5.20 (d, *J* = 6.5 Hz,

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[22] (a) J. C. Dalton, P. A. Wriede, and N. J. Turro, *J. Amer. Chem. Soc.*, in press; (b) N. J. Turro and P. A. Wriede, *ibid.*, in press.

[23] P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 21 (1967); J. A. Barltrop and J. D. Coyle, *Tetrahedron Lett.*, 3235 (1968).

[24] P. Dunion and C. N. Trumbore, *J. Amer. Chem. Soc.*, **87**, 4211 (1965); C. C. Badcock, M. J. Perona, G. O. Pritchard, and B. Rickborn, *ibid.*, **91**, 543 (1969), and references therein.

[25] H. O. Denschlag and E. K. C. Lee, *ibid.*, **89**, 4795 (1967); D. McDaniel and N. J. Turro, unpublished results.

[26] N. J. Turro, *Photochem. Photobio.*, **9**, 555 (1969).

[27] P. J. Wagner, *J. Amer. Chem. Soc.*, **89**, 2503 (1967); N. C. Yang and S. P. Elliott, *ibid.*, **90**, 4194 (1968).

[28] R. Simonaitis, G. W. Cowell, and J. N. Pitts, Jr., *Tetrahedron Lett.*, 375 (1967).

1 H) ring hydrogen α to nitrile and oxygen, 4.12 (d, J = 6.5 Hz, 1 H) ring hydrogen α to nitrile, 2.50–1.50 (broad, 8 H) five-membered-ring methylenes. No parent ion was observed in the mass spectrum of **12**, but fragments were observed at m/e 133 (28% of base peak), 107 (13), 106 (9), 105 (5), 85 (7), 84 (74), 80 (12), 79 (19), 78 (42), 67 (25), 56 (34), 55 (100), and 41 (48).

Anal. Calcd for $C_9H_{10}ON_2$: C, 66.70; H, 6.18; N, 17.30. Found: C, 66.90; H, 6.46; N, 17.66.

Adduct **13** had a retention time of 6 min at 175° and collected as a colorless oil: infrared spectrum λ_{max} (CCl_4) 2232 (CN), 1018 and 980 cm^{-1} (oxetane ring); nmr δ 5.28 (d, J = 8.5 Hz, 1 H), ring hydrogen α to nitrile and oxygen, 4.27 (d, J = 8.5 Hz, 1 H), ring hydrogen α to nitrile, 2.50–1.60 (broad, 8 H) five-membered-ring methylenes.

Anal. Calcd for $C_9H_{10}ON_2$: C, 66.70; H, 6.18; N, 17.30. Found: C, 66.60; H, 6.19; N, 17.43.

Adduct **14** had a retention time of 1.5 min at 175° and was found by nmr to be a mixture of two isomeric forms. The adducts collected as a viscous oil: infrared λ_{max} (CCl_4) 2232 (CN), 1379 (methyl) and 1005 cm^{-1} (oxetane ring); nmr δ 5.18 (d, J = 6.8 Hz) and 5.13 (d, J = 6.5 Hz) ring hydrogens α to nitrile and oxygen, 3.88 (d, J = 6.8 Hz) and 3.83 (d, J = 6.5 Hz) ring hydrogens α to nitrile, 1.59 (s) methyl on quarternary carbon, 2.18–1.20 (broad) methylenes, 1.03 (t) methyl next to methylene. The mass spectrum of **14** contained no parent ion, but loss of methyl was observed at m/e 149 (2.2% of base peak). Other fragments were found at m/e 121 (45), 86 (11), 78 (24), 71 (28), 68 (20), 58 (39), and 43 (100).

Anal. Calcd for $C_9H_{12}ON_2$: C, 65.95; H, 7.31; N, 17.10. Found: C, 65.89; H, 7.31; N, 17.29.

Adduct **15** had a retention time of 3.5 min at 175° and was also found to be a mixture of two isomeric forms: infrared spectrum λ_{max} (CCl_4) 2232 (CN), 1379 (methyl), 1005 and 900 cm^{-1} (oxetane ring); nmr δ 5.29 (d, J = 9.0 Hz) and 5.22 (d, J = 9.0 Hz) ring hydrogens α to nitrile and oxygen, 4.00 (d, J = 9.0 Hz) and 3.96 (d, J = 9.0 Hz) ring hydrogens α to nitrile, 1.69 (s) methyl, 1.49 (s) methyl, 2.20–2.15 (m) methylenes and 0.99 (t) methyl next to methylene.

Anal. Calcd for $C_9H_{12}ON_2$: C, 65.95; H, 7.31; N, 17.10. Found: C, 65.93; H, 7.27; N, 17.16.

Preparation of Adduct 19.—Maleic anhydride (0.514 g) was dissolved in 2.5 g of acetone and irradiated through Pyrex for 17 hr. After photolysis, 0.102 g of an insoluble solid precipitated from the solution. Removal of the acetone under vacuum and addition of ether to the resulting colored solution led to the formation of a white precipitate, which was collected, washed with ether and dried. After sublimation (1 mm and 60°) the white solid had a melting point of 97–98°; nmr δ 5.25 (d, J = 5.5 Hz, 1 H) ring hydrogen α to ring oxygen, 3.90 (d, J = 5.5 Hz, 1 H) ring hydrogen β to ring oxygen, 1.67 (s, 3 H) methyl and 1.42 (s, 3 H) methyl; infrared spectrum λ_{max} (KBr) 1852 and 1786 (anhydride), 1376 and 1366 (methyl), 1093, 1002, and 921 cm^{-1} (oxetane ring). The mass spectrum of **19** contained no molecular ion, but did contain fragments at m/e 141 (0.5% base peak), 85 (6), 84 (100), 83 (74), 56 (24), 55 (46), 54 (14), 43 (88), 41 (46) and 39 (31).

Anal. Calcd for $C_7H_8O_4$: C, 53.84; H, 5.13. Found: C, 53.64; H, 5.01.

Preparation of 1-Methoxy-1-butene.—An isomeric mixture of 1-methoxy-1-butenes was prepared by the method of Martin, *et al.*[20] A catalytic amount (0.5 ml) of H_3PO_4 (85%) was added to 110 g of n-butyraldehyde dimethyl acetal[29] and the mixture was distilled through a 20-in. Vigreux column. The distillate boiling between 60 and 70° was collected over K_2CO_3, then washed with water several times to remove methanol. The crude mixture of olefins was dried over K_2CO_3 and distilled. The fraction boiling between 72 and 75° was collected. The yield was 35 g (43%) of a 60:40 mixture of *cis* and *trans* olefins. Samples of the pure isomers were obtained by preparative vpc on a 25% $AgNO_3$–ethylene glycol column (10-ft Chrom P) at 50°. *cis*-1-Methoxy-1-butene distilled between 71 and 72° (n^{20}D 1.4011): nmr δ 5.72 (d of t, J = 6.3 and 7.0 Hz, 1 H) olefinic proton α to methoxyl, 4.24 (d of t, J = 6.3 and 7.0 Hz, 1 H) olefinic proton α to ethyl group, 3.50 (s, 3 H) methoxyl, 2.03 (m, 2 H) methylene, 0.92 (t, J = 7.0 Hz, 3 H) methyl. *trans*-1-Methoxy-1-butene distilled between 75 and 76° (n^{20}D 1.4010); nmr δ 6.10 (d of t, J = 13.2 and 7.2 Hz, 1 H) olefinic proton α to methoxyl, 4.55 (d of t, J = 13.2 and 7.2 Hz, 1 H) olefinic proton α to ethyl group, 3.37 (s, 3 H) methoxyl, 1.90 (m, 2 H) methylene, 0.95 (t, J = 7.0 Hz, 3 H) methyl.

Preparation and Isolation of Adducts 20–23.—1-Methoxy-1-butene (10 ml) (60:40, *cis–trans*) was dissolved in 200 ml of acetone and irradiated through a Vycor well with a 450-W medium pressure mercury lamp. The solution was placed in a jacket that fit around the Vycor well and was stirred by a slow stream of nitrogen gas. After 6 hr of irradiation, the acetone and residual olefin were distilled off, leaving behind 8.96 g of a sweet smelling oil.

The oil was analyzed by vpc on a 6-ft 20% Carbowax 20M (Chrom P) column at 100°. Adduct **22** collected as a colorless oil: infrared spectrum λ_{max} (liquid film) 2899 (CH), 1370 (methyl), and 948 cm^{-1} (oxetane ring); nmr δ 5.00 (d, J = 6 Hz, 1 H) ring hydrogen α to methoxyl and ring oxygen, 3.26 (s, 3 H) methoxyl, 2.47 (d of t, J = 6 and 8 Hz, 1 H) ring hydrogen α to ethyl group, 1.57 (m, 2 H) methylene, 1.33 (s, 3 H) methyl, 1.27 (s, 3 H) methyl, and 0.81 (t, J = 7 Hz, 3 H) methyl of ethyl group.

Adduct **20** collected as a colorless oil: infrared spectrum λ_{max} (liquid film) 1370 (methyl), and 939 cm^{-1} (oxetane ring); nmr δ 4.40 (q, J = 6.5 Hz, 1 H) ring hydrogen α to ring oxygen, 3.87 (d, J = 6.5 Hz, 1 H) ring hydrogen β to methoxyl, 3.24 (s, 3 H) methoxyl, 1.52 (m, 2 H) methylene, 1.35 (s, 3 H) methyl, 1.26 (s, 3 H) methyl, and 0.87 (t, J = 7.0 Hz, 3 H) methyl of ethyl group.

Adducts **21** and **23** could not be separated from one another by vapor phase chromatography. A mixture of the two adducts had the following spectral characteristics: infrared spectrum λ_{max} (liquid film) 1361 (methyl), 952 and 934 cm^{-1} (oxetane ring); nmr δ 4.70 (d, J = 4 Hz, 1 H) ring hydrogen α to methoxyl and ring oxygen in **23**, 4.10 (q, J = 5.5 Hz, 1 H) ring hydrogen α to ring oxygen in **21**, 3.40 (d, J = 5.5 Hz, 1 H) ring hydrogen α to methoxyl in **21**, 3.28 (s, 3 H) methoxyl, 3.21 (s, 3 H) methoxyl, 2.15 (d of t, J = 4 and 8 Hz, 1 H) ring hydrogen α to ethyl group in 23, 1.60 (m) methylene, 1.35 (s), 1.28 (s), 1.22 (s) methyls, 0.89 (t, J = 6.5 Hz) and 0.87 (t, J = 7.0 Hz) methyls of ethyl group.

A pure sample of adduct **21** was obtained by treating the crude mixture of four oxetanes with 0.1 M HCl for 30 min. After extracting the reaction mixture with ether and washing the ether solution with water, the solvent was removed and the remaining oil was subjected to vapor phase chromatography. Adduct **21** was collected as a colorless oil: nmr δ 4.10 (q, J = 5.5 Hz, 1 H), 3.40 (d, J = 5.5 Hz, 1 H), 3.21 (s, 3 H), 1.57 (m, 2 H), 1.28 (s, 6 H), 0.89 (t, J = 7.0 Hz, 3 H).

The mass spectrum of a mixture of the four isomeric oxetanes shows no parent ion. The base peak is at m/e 71 (100%) and other fragments are found at m/e 86 (54), 84 (19), 69 (30), 55 (15), 43 (46), 41 (53).

Anal. Calcd for $C_8H_{16}O_2$: C, 66.66; H, 11.11. Found: C, 66.18; H, 10.85.

Registry No.—**6**, 746-42-1; **7**, 928-53-0; **10**, 21537-72-4; **11**, 21537-73-5; **12**, 21537-74-6; **13**, 21537-75-7; **14**, 21537-76-8; **15**, 21537-77-9; **19**, R_1, R_2 = CH_3, 21545-07-3; **20**, 21537-78-0; **21**, 21537-79-1; **22**, 21537-80-4; **23**, 21537-81-5; *cis*-1-methoxy-1-butene, 10034-12-5; *trans*-1-methoxy-1-butene, 10034-13-6; maleic anhydride, 108-31-6.

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[29] I. Chalpanova and A. Nemwrovskii, *Chem. Abstr.*, **54**, 24358a (1954).