12

J.C.S. Perkin I

Synthetic Studies of Carbohydrate Derivatives by Photochemical Reactions. Part 16.[1] Synthesis of DL-Apiose Derivatives by Photochemical Cycloaddition of 1,3-Dihydroxypropan-2-one Derivatives with Ethenediol or Ethenol Derivatives
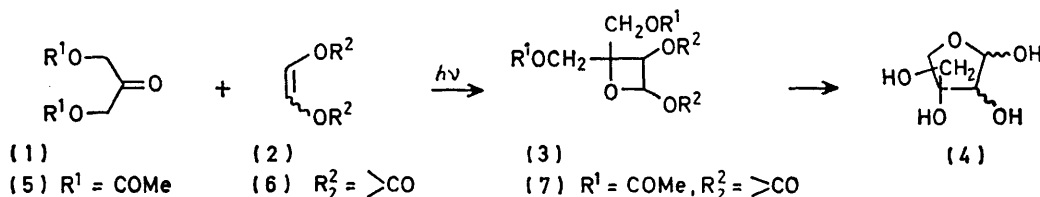
By **Younosuke Araki,*** **Jun-ichi Nagasawa,** and **Yoshiharu Ishido,** Department of Chemistry, Faculty of Science, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan

Irradiation of a benzene solution of 1,3-diacetoxypropan-2-one (5) and 1,3-dioxol-2-one (6) with a high-pressure mercury lamp gave a photocycloaddition product, (7-acetoxymethyl-3-oxo-2,4,6-trioxabicyclo[3.2.0]heptan-7-yl)-methyl acetate (7) (55% yield). Similar photocycloadditions of (5) with (Z)-vinylene diacetate (23), with (Z)-2-(benzyloxy)vinyl acetate (25), with 2,3-dihydro-1,4-dioxin (27), with vinyl acetate (28), with isopropenyl acetate (29), with ethoxyethene (30), and with 1,1-diethoxyethene (43) afforded cis-4,4-bis(acetoxymethyl)oxetan-2,3-diyl diacetate (31) (46% yield) and the trans-isomer (32) (49% yield); 2,2-bis(acetoxymethyl)-4-(benzyloxy)-oxetan-3-yl acetate (33) (composed of the two isomers; 11% and 26% yields) and 4,4-bis-(acetoxymethyl)-3-benzyloxy)oxetan-2-yl acetate (38) (composed of the two isomers; 11% and 9% yields); (8-acetoxymethyl-2,5,7-trioxabicyclo[4.2.0]oct-8-yl)methyl acetate (34) (25% yield); 2,2-bis(acetoxymethyl)oxetan-3-yl acetate (35) (28% yield) and 4,4-bis(acetoxymethyl)oxetan-2-yl acetate (39) (15% yield); 2,2-bis(acetoxymethyl)-3-methyloxetan-3-yl acetate (36) (55% yield); (2-acetoxymethyl-3-ethoxyoxetan-2-yl)methyl acetate (37) (53% yield); and (2-acetoxymethyl-3,3-diethoxyoxetan-2-yl)methyl acetate (44) (48% yield) and ethyl 4-acetoxy-3-acetoxymethyl-3-hydroxybutyrate (45) (19% yield), respectively. The reaction of (5) with (43) was also induced thermally to give ethyl 4-acetoxy-3-(acetoxymethyl)coronate (46) (24% yield) in addition to (45) (20% yield). Photocycloaddition of diethyl mesoxalate (21) with (6) gave diethyl 3-oxo-2,4,6-trioxabicyclo[3.2.0]heptane-7,7-dicarboxylate (22) (23% yield). On the other hand, the reactions of 1,3-dimethoxy- (8) and 1,3-bis(benzyloxy)-propan-2-one (13) respectively with (6) afforded none of the expected photocycloadducts, but several products due to the intramolecular hydrogen abstraction from (8) and (13). The reaction of 2,2-dimethyl-1,3-dioxan-5-one (2) with (6) was also accompanied by predominant decomposition of (20).

WE have reported a series of synthetic studies of carbo-hydrate derivatives by photochemical additions to enose derivatives.[1] We now report the synthesis of branched-chain sugar derivatives by photocycloaddition of ketonic species to alkene derivatives, which has recently been briefly communicated.[2]

RESULTS AND DISCUSSION

In the first place, the reaction was performed by use of the most easily available materials, i.e. 1,3-diacetoxy-propan-2-one (5) and 1,3-dioxol-2-one (6); (5) was subjected to the reaction with (6) (2 equiv.) in a variety of solvents ‡ under irradiation with a high-

pressure mercury lamp. The results thus obtained and the conditions used are summarized in Table 1. The reactions in all the solvents shown in the Table and that without solvent afforded the desired oxetan, i.e. (7-acetoxymethyl-3-oxo-2,4,6-trioxabicyclo-[3.2.0]heptan-7-yl)methyl acetate (4,4'-di-O-acetyl-1,2-O-carbonyl-DL-apiotetranose) (7). Among the solvents, benzene was shown to give the highest yield, calculated on the amounts of consumed (5). The reactions in the solvents other than benzene were accompanied by side-reactions (see Table 1). On the other hand, some reactions gave no (7), according to t.l.c. analysis, but only precipitated polymers of (6), this occurred in 1,4-dioxan, tetrahydrofuran, 1,2-dimethoxyethane, methanol, and isopropyl alcohol; the results are not shown in Table 1.

The Paterno–Büchi reaction is known to afford oxetans through the photocycloaddition reaction of carbonyl compounds to alkenes.[3] However, the reaction has seldom been applied to synthesis of natural products, although well studied from the standpoint of synthetic and mechanistic aspects.[4] This reaction should afford DL-apiose † (4) if we use 1,3-dihydroxypropan-2-one derivatives (1) as carbonyl species and ethene-1,2-diol derivatives (2) as alkenic species in combination with subsequent hydrolysis of the resulting oxetan derivatives (3). On the basis of such an assumption, we undertook an investigation of oxetan formation via photocyclic addition for the synthesis of DL-apiose derivatives.

† There have been a number of papers reported on the synthesis of DL-apiose, and the details are available in a review.[5] Recently, Ho [6] reported a novel and simple synthetic method. However, no synthetic method involving photochemical reaction, has been previously reported.

‡ The solubility of both (5) and (6) in cyclohexane was too low for their reactions to be investigated in this solvent.

A solution containing only (6) afforded no precipitates on irradiation under the same conditions. Therefore the polymerization of (6) is presumably initiated by radical species arising from hydrogen abstraction from

TABLE 1

Examination of solvent effects on the photocycloaddition of 1,3-diacetoxypropan-2-one (5) to 1,3-dioxol-2-one (6) [a]

	Conditions		Yield	
Entry	Solvent	Time (h)	(7) [c]	(5)
1	Neat [b]	26	23 (55)	58
2	Acetonitrile [b]	15	18 (47)	62
3	Pyridine [d]	15	6 (55)	89
4	Ethyl acetate [b]	15	27 (43)	37
5	Diethyl carbonate [b]	15	31 (49)	37
6	t-Butyl alcohol [b]	15	29 (59)	51
7	t-Butyl alcohol [b]	30	30 (45)	36
8	Acetic acid [b]	15	29 (59)	51
9	Acetic acid [b]	30	37 (38)	3
10	Benzene	15	33 (72)	54
11	Benzene [e]	30	46 (63)	27

[a] Except for Entry 1, all the reactions were performed using (5) (0.25M) and (6) (0.5M) irradiated with a high-pressure mercury lamp (450 W). Resulting mixtures were separated by chromatography on a column of silica gel. [b] Polymers of (6) were formed. [c] Yields in parentheses are of those based on the amount of (5) consumed. [d] Much discolouration occurred. [e] A trace amount of (2-oxo-5-phenyl-1,3-dioxolan-4-yl)methyl acetate (19) was produced.

solvent molecules by (5) in the excited triplet state. Incidentally, no (7) could be detected in the reaction in acetone. From the results described above, benzene was concluded to be the most appropriate solvent for the reaction since its hydrogen is hardly susceptible to the

TABLE 2

Effect of reaction time, concentration, and the proportions of (5) and (6), on the photocycloaddition reaction [a]

	Concentration/M		Reaction time/h	Yield (%)		
Entry [b]	(5)	(6)		(7) [c]	(19)	(5)
1	0.25	0.5	10	13 (72)		82
2	0.25	0.5	20	27 (77)		65
3	0.25	0.5	40	34 (67)	1	49
4	0.25	0.5	80	40 (67)	1	42
5	0.25	0.5	15	10 (71)		86
6	0.25	0.5	40	19 (46)		59
7	0.5	1.0	40	23 (58)		60
8	1.0	2.0	40	14 (64)		78
9	1.5	3.0	40	12 (57)		79
10	0.25	0.5	15	23 (66)		65
11	0.25	0.5	30	38 (68)	1.5	44
12	0.1	0.5	20	51 (78)		38
13	0.1	0.5	30	55 (81)	2	32
14	0.25	0.5	15.5	34 (69)	1	51
15 [d]	0.25	0.5	15.5	33 (89)		63

[a] All the reactions of (5) with (6) were performed under irradiation with a high-pressure mercury lamp (450 W), and the resulting mixtures were then chromatographed on a column of silica gel. [b] The reactions of Entries 1—4, 5—9, and 10—15 were performed together, respectively, to standardize the luminous intensity as far as possible. [c] The yields in parentheses are of those based on the amount of (5) consumed. [d] This reaction was carried out in the presence of biphenyl (0.5M).

abstraction reaction. Consequently, benzene was used in the reactions which will be described below.

In the second place, conditions for the reaction of (5) with (6) were investigated with respect to concentration,

proportions, and reaction times; the results are summarized in Table 2. As seen from Entries 1—4, the yield of (7) was improved on prolonging the reaction time. Incidentally, [1]H n.m.r. spectroscopy showed the resulting mixture, after irradiation for 80 h (Entry 4), to involve 2.6-fold mol of (6) to (5). Moreover, (7) (81%) was recovered on 82 h-irradiation of a 0.1M benzene solution under the same condition as those in Entries 1—4. Therefore, it may be concluded that the degradation reaction of (7) is considerably slower than its formation reaction. On increasing the concentration of (5) and (6) provided their ratio was maintained at 1 : 2 (see Entries 5—9), the reaction was found to be slowed down when the concentration of (5) exceeded 0.5M; this may be due to depression of photoefficiency of the reaction with the increase in the concentration. Moreover, (7) was obtained in comparatively good yield on performing the reaction by reducing the proportion of (5) to (6) (see Entries 10—13). Furthermore, degradation of (5) was reduced and its conversion into (7) was improved when biphenyl was added to the system, although the yield of (7) did not vary (see Entries 14 and 15). Incidentally, a small amount of (2-oxo-5-phenyl-1,3-dioxolan-4-yl)-methyl acetate (19) was obtained as a by-product. The structure of (7) was assigned by i.r. (see Experimental


(19)
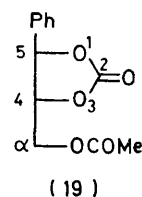
section) and [1]H n.m.r. spectral data (see Table 3), i.e. (1) the H-1 and H-2 signals appeared at δ 6.24 and 5.35 with $J_{1.2}$ value of 4.0 Hz; (2) two methylene proton signals were present both with an AB splitting pattern; and (3) the i.r. spectrum had an absorption band at 1 825 cm^{-1}, which corresponds to a cyclic carbonate. The δ-values for H-1 and H-2, and the $\nu_{C=O}$ value are consistent with those [7] for known oxetan derivatives prepared from the photochemical reaction of a ketone with (6). This assignment was proved by isolation of DL-apiose (4) in 90% yield by treating (7) with strongly basic ion-exchange resin [Amberlite IRA-400 (OH$^-$)] in methanolic water; the resulting syrupy (4) was identified as its phenylosazone.[8] The structure of (19) was similarly assigned as above, i.e. (1) the [1]H n.m.r. spectrum had phenyl signals at δ 7.42, a 3-proton acetyl signal at δ 2.14, a 1-proton doublet at δ 5.44, a 1-proton double double doublet at δ 4.74, and two 1-proton double doublets at δ 4.45 and 4.38; and (2) its i.r. spectrum gave absorption bands at $\nu_{C=O}$ 1 805 and 1 745 cm^{-1}. One geometrical isomer was obtained, although two isomers are possible for (19).

On the basis of the above results, the reactions of (6) with some other 1,3-dihydroxypropan-2-one derivatives (1) were undertaken. Those with 1,3-dimethoxy- (8) and 1,3-bis(benzyloxy)-propan-2-one (13) gave no oxetan

derivatives at all, but mainly products arising from the intramolecular hydrogen abstraction of (8) and (13), respectively. In the reaction of (8), 3-methoxymethyl-oxetan-3-ol (9), 2,4,6-trioxabicyclo[3.2.0]heptan-3-one (10), 4-acetyl-5-phenyl-1,3-dioxolan-2-one (11), and cis-transoid-cis-3,5,8,10-tetraoxatricyclo[5.3.0.0^{2,6}]-decane-4,9-dione (12) were obtained. In the reaction of

decomposition products. The structure of (9) was proved by its ¹H n.m.r. spectrum, which showed two 2-proton doublets at δ 4.48 and 4.64. Compound (9) was obtained as a distillate [15% yield, containing 13% of (8)] from the resulting mixture from the irradiation of (8) in a benzene solution; the elemental analysis was satisfactory for its structure [(8) and (9) have the same
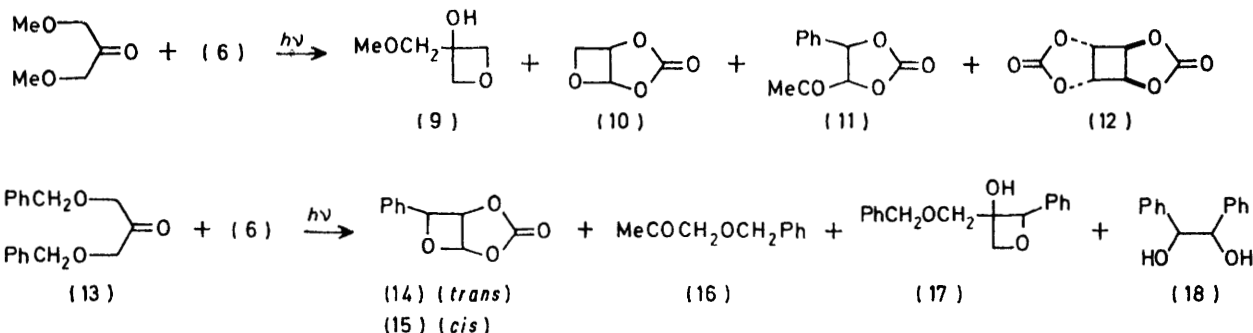
(13), on the other hand, trans- (14) and cis-7-phenyl-2,4,6-trioxabicyclo[3.2.0]heptan-3-one (15), 1-benzyloxy-propan-2-one (16), 3-benzyloxymethyl-2-phenyloxetan-3-ol (17), and 1,2-diphenyl-1,2-ethanediol (18) were obtained. The resulting mixtures from both above reactions further contained other products other than those above described; although these were impossible to isolate or identify, they suggest that the reactions involve complex reaction pathways to give mainly

molecular formula]. The structure of (10) was proved by (1) the ¹H n.m.r. spectrum which had a 1-proton doublet at δ 6.30, two 1-proton double doublets at δ 4.97 and 4.75, and a double double doublet at δ 5.45; and (2) the i.r. spectrum showed an absorption band specific for carbonates (1 800 cm⁻¹). The structural determination of (11) was also based on spectroscopic data; i.e. (1) the ¹H n.m.r. spectrum showed a 5-proton singlet at δ 7.42, a 3-proton singlet at δ 2.43, and two mutually coupled

TABLE 3

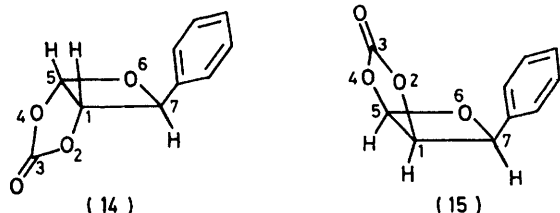¹H n.m.r. spectral data for the oxetan derivatives obtained [a]

Compound	R¹	R²	R³	H-1	H-2	H-4	H-5	COMe	Other	$J_{1,1}$	$J_{1,2}$	$J_{2,2}$	$J_{4,4}$	$J_{5,5}$
(7)	OCO₂		H	6.24 (d)	5.35 (d)	4.41 (d), 4.21 (d)	4.35 (d), 4.24 (d)	2.16 (3 H), 2.13 (3 H)			4.0		12.5	12.5
(31)	OAc	OAc	H	6.50 (d)	5.59 (d)	4.53 (d), 4.47 (d)	4.43 (d), 4.23 (d)	2.16 (3 H × 2), 2.13 (3 H), 2.09 (3 H)			5.0		12.0	12.5
(32) [b]	OCH₂Ph	OAc	H	6.40 (d)	5.36 (d)	4.50 (d), 4.23 (d)	4.45 (d), 4.30 (d)	2.15 (3 H), 2.14 (3 H), 2.12 (3 H), 2.11 (3 H)			3.5		12.5	12.0
(33a)	OCH₂Ph	OAc	H	5.52 (d), 5.29 (d)		c	c	2.06 (3 H × 3)	Ph 7.33 (s) CH₂ [e]		3.5		d	d
(33b)	OCH₂Ph	OAc	H	5.57 (d), 5.44 (d)		c	c	2.06—2.13 (3 H × 3)	Ph 7.31 (s) CH₂ 4.54 (s)		5.0		d	d
(38a)	OAc	OCH₂Ph	H	6.40 (d)	4.58 (d)	4.64 (d), 4.43 (d)	4.30 (d), 4.12 (d)	2.13 (3 H), 2.09 (3 H), 2.06 (3 H)	Ph 7.31 (s) CH₂ 4.52 (s)		4.5		12.5	12.5
(38b)	OAc	OCH₂Ph	H	6.25 (d)	4.33 (d)	4.53 (d), 4.35 (d)	4.30 (d), 4.14 (d)	2.10 (3 H), 2.09 (3 H), 2.06 (3 H)	Ph 7.32 (s) CH₂ 4.58 (s)		3.5		12.5	12.5
(34) [b]	OCH₂CH₂O		H	5.64 (d)	4.56 (d)	4.43 (s)	4.32 (s)	2.11 (3 H), 2.08 (3 H)	OCH₂CH₂O 3.5—4.0 (3 H) (m) 4.1—4.6 (1 H) (m)		4.0			
(35) [b]	H	OAc	H	4.73 (t), 4.50 (dd)	5.47 (t)	4.44 (d), 4.34 (d)	4.37 (d), 4.20 (d)	2.14 (3 H), 2.09 (3 H × 2)		7.5	6.5, 6.0		12.5	12.5
(39)	OAc	H	H	6.39 (dd)	2.93 (dd), 2.54 (dd)	4.32 (s)	4.27 (s)	2.14 (3 H × 3)			5.5, 4.0	13.0		
(36) [b]	H	OAc	Me	4.79 (d), 4.49 (d)		4.52 (s)	4.35 (s)	2.10 (3 H × 2), 2.06 (3 H)	Me 1.72 (s)	9.5				
(37)	H	OEt	H	e	e	e	4.26 (br, s)	2.12 (3 H), 2.08 (3 H)	CH₂ 3.46 (q) Me 1.52 (t)	d	d		d	$J_{CH_2-CH_3}$ 7.0
(44)	H	OEt	OEt	4.49 (s)		4.42 (s)	4.42 (s)	2.08 (3 H × 2)	CH₂ 3.50 (q) Me 1.23 (t)					$J_{CH_2-CH_3}$ 7.0

[a] These spectral data were obtained with a Varian T–60 apparatus for solutions in deuteriochloroform with tetramethylsilane as internal standard. Locants for each assigned proton are based on the numbering of the structure of
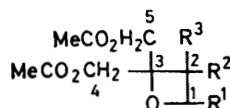

[b] The chemical shifts were also determined through the INDOR technique with a Varian EM–390 apparatus. c δ 4.0—5.0; assignment was impossible due to the mixture of isomers. d Not determined due to ambiguity in determining chemical shifts. e The signals appeared as an unresolvable multiplet with δ 4.2—4.8.

1-proton doublets at δ 5.68 and 4.76; and (2) the i.r. spectrum showed characteristic absorption bands at 1 800 and 1 720 cm⁻¹, respectively. Compound (12) was identical with the compound prepared according to the method reported.[9] Compounds (14) and (15) were

(14)   (15)

assigned as oxetan derivatives produced by the addition of benzaldehyde to (6) on the basis of their spectral data; *i.e.* their i.r. spectra had specific absorption bands at 1 815 and 1 805 cm⁻¹, respectively, and their ¹H n.m.r. spectra gave 5-proton phenyl signals at δ 7.40 and 7.38,

thus be proved by the values of $\delta_{(15)} - \delta_{(14)}$ for H-1 (0.41 p.p.m.) and those for H-5 (0.27 p.p.m.). For the H-7 signals, these should only slightly differ in chemical shift since they are under the anisotropic effect to almost the same extent, giving a $\delta_{(15)} - \delta_{(14)}$ value of −0.09. Therefore, H-5 and H-7 were assigned to the signals at δ 5.79 and 6.42 for (14), and those at δ 6.06 and 6.33 for (15), respectively. The structure of (16) was confirmed by comparison with an authentic sample prepared according to a reported method.[10] Although a pure sample could not be obtained, the structure of (17) was determined *via* ¹H n.m.r. spectroscopy, *i.e.* two 5-proton phenyl signals at δ 7.38 and 7.35, a 1-proton singlet at δ 5.67, a 2-proton singlet at δ 4.66, and two pairs of AB 1-proton doublets at δ 4.64 and 4.56, and at δ 3.90 and 3.72. From the ¹H n.m.r. spectrum, compound (18) was obtained as a mixture of racemic and *meso*-isomers, from which we could isolate the *meso*-isomer as a crystalline sample; the m.p., and i.r. and ¹H n.m.r. spectra were
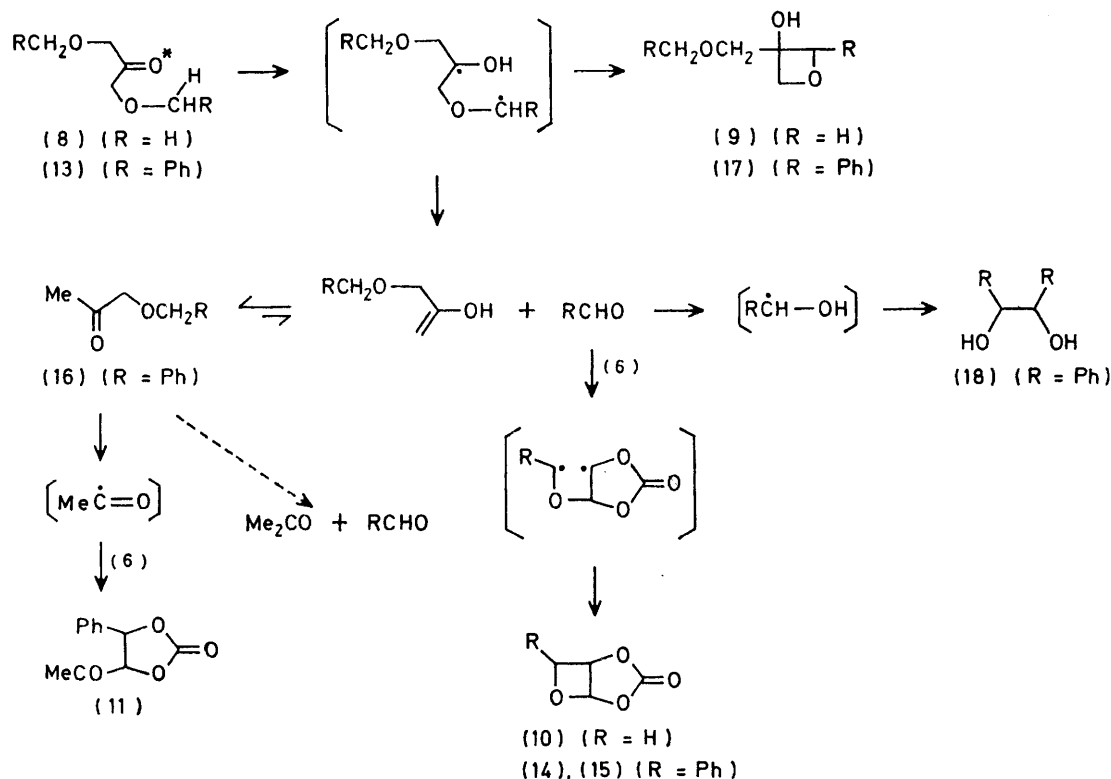
respectively, in addition to 1-proton signals at δ 5.11 (dd), 5.79 (d), and 6.42 (d) for (14), and 5.52 (dd), 6.06 (d), and 6.33 (d) for (15). The *cis–trans* isomerism of (14) and (15) was proved by ¹H n.m.r. spectroscopy, on the basis of the assumption that for their H-1 and H-5 signals, those *cis* to the phenyl group in (14) are less deshielded than those *trans* to the phenyl group in (15), due to the anisotropic effect of the phenyl group. Since H-1 is closer to the phenyl group than H-5, the anisotropic effect should make the difference in chemical shifts of the H-1 protons larger than that of H-5 protons. This assumption may

identical with those of an authentic sample prepared according to a known method.[11]

The mechanism of the reactions of (6) with (8) or with (13) can be assumed to be as follows based on the structures of the products obtained. All the results may be explained by assuming Norrish Type II, *i.e.* intramolecular hydrogen abstraction, reaction of (8) or (13) in the n→π* excited state, accompanied by ring-closure, bond-fission, and addition reactions. Product (12) might be formed through the dimerization of (6), photosensitized by (8) or its decomposition products.[9]

Therefore, the ketonic species having hydrogen susceptible to abstraction at the γ-position are found to undergo predominantly Norrish Type II reactions under the conditions used, and are thus unsuitable as substrates for the Paterno–Büchi reaction.

On the basis of the above results we subsequently performed the photochemical reaction of (6) with 2,2-dimethyl-1,3-dioxan-5-one (20), which is not susceptible to the intramolecular hydrogen abstraction reaction. On irradiation of (20) (0.25M) with (6) (2 equiv.) for 6 h, t.l.c. of the resulting mixture showed the complete consumption of (20); however, the products could not be isolated due to the complexity of the mixture, which made their chromatographic separation impossible. The irradiation of (20) itself also gave a mixture, giving the same pattern on t.l.c. as that obtained in the above reaction. The above reaction may thus predominantly involve the decomposition reaction of (20), although we

(20)   (21)   (22)
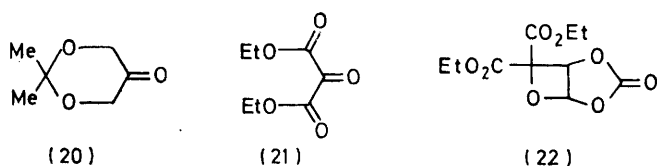
could not isolate all the products for unambiguous evidence.

With this result, the reaction of (6) with diethyl mesoxalate (21) was performed; it has a low E_T of 54 kcal mol^{-1},[12] which may facilitate the formation of the corresponding oxetan derivative. As expected, the

and the ^{1}H n.m.r. spectrum, which showed two 1-proton doublets (J 3.5 Hz) at δ 5.77 and 6.37, and two kinds of methylene proton signals. It should be noted here that chromatographic treatment of (22) in the same manner as above gave (22) in 60% yield. This may indicate that the low yield of (22) arises from its decomposition during the chromatographic separation, although we could not identify the decomposition products.

These results subsequently prompted us to perform the photochemical reaction of ethenediol derivatives and ethenol derivatives other than (6), with (5) as the ketonic species. The results thus obtained are summarized in Table 4. The reaction of (5) with (Z)-vinylene diacetate (23) gave cis-4,4-bis(acetoxymethyl)oxetan-2,3-diyl diacetate (1,2,4,4'-tetra-O-acetyl-α-DL-apiotetranose) (31) and the trans-isomer (β-anomer) (32) in high yield in addition to a small amount of a product which was assumed to be 2-(1,2-diacetoxyethoxy)propenylene diacetate (41). Moreover, (E)-vinylene diacetate (24), the isomer of (23), was obtained as well as recovered (23). Incidentally, the irradiation of (23) for 80 h resulted in only 6% isomerization into (24); this may indicate the participation of (5) in the isomerization. The reaction of (5) with 2-(benzyloxy)vinyl acetate * (25, 26) gave 2,2-bis(acetoxymethyl)-4-(benzyloxy)oxetan-3-yl acetate (benzyl 2,4,4'-tri-O-acetyl-DL-apiotetranoside) (33) and 4,4-bis(acetoxymethyl)-3-benzyloxyoxetan-2-yl acetate (1,4,4'-tri-O-acetyl-2-O-benzyl-DL-apiotetranose) (38) as a mixture of two isomers (anomers), respectively. In this case, the isomerization between (25) and (26) was also confirmed to have occurred, i.e. the amount of

Entry	Derivative	Conditions		Yield (%)				(5)
		Concentration of (5)/M	Time/h	Product				
1	(Z)-Vinylene diacetate (23)	0.25	40 [b]	(31)	37	(32)	34	27
2	(23)	0.25	80 [c]	(31)	46	(32)	49	
3	(Z)-2-(Benzyloxy)vinyl acetate [d] (25) [(E)- (26)]	0.25	30 [e]	(33)	11 [f] + 26 [f]	(38)	11 [f] + 9	38
4	2,3-Dihydro-1,4-dioxin (27)	0.25	30	(34)	25			49
5	Vinyl acetate (28)	0.25	15 [g]	(35)	15	(39)	6	54
6	(28)	0.1	20 [g]	(35)	28	(39)	15	45
7	Isopropenyl acetate (29)	0.25	15	(36)	33			46
8	(29)	0.1	20	(36)	55			37
9	Ethoxyethene (30)	0.25	30	(37)	48			32
10	(30)	0.1	30	(37)	53			14

irradiation of (21) with 2 equiv. (6) for 6—7 h gave a mixture involving no (21) (t.l.c.), and chromatographic separation on a column of silica gel afforded a 23% yield of diethyl 3-oxo-2,4,6-trioxabicyclo[3.2.0]heptane-7,7-dicarboxylate (diethyl 1,2-O-carbonyl-DL-apiotetrandiuronate) (22). The structure of (22) was confirmed from the i.r. spectrum, which showed the absorption band at 1 840 cm^{-1} specific for cyclic carbonate esters,

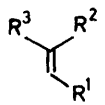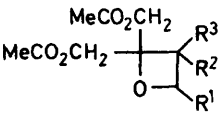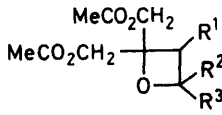recovered (26) increased; exceeding that in the starting material (154 mg→372 mg; see Experimental section). Furthermore, the reaction of (5) with 2,3-dihydro-1,4-dioxin (27), with vinyl acetate (28), with isopropenyl acetate (29), and with ethoxyethene (30), gave (8-acetoxymethyl-2,5,7-trioxabicyclo[4.2.0]oct-8-yl) methyl acetate (4,4'-di-O-acetyl-1,2-O-ethylene-DL-
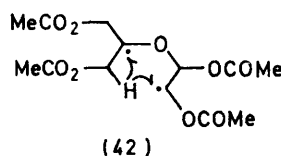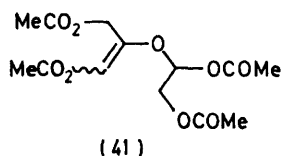
* (Z) : (E) [(25) : (26)] = 92 : 8.

apiotetranose) (34); 2,2-bis(acetoxymethyl)oxetan-3-yl acetate (2,4,4'-tri-O-acetyl-1,3-anhydro-DL-apiitol) (35) and 4,4-bis(acetoxymethyl)oxetan-2-yl acetate (1,4,4'-tri-O-acetyl-2-deoxyapiotetranose) (39); 2,2-bis-(acetoxymethyl)-3-methyloxetan-3-yl acetate (2,4,4'-tri-O-acetyl-1,3-anhydro-2-C-methyl-DL-apiitol) (36); and (2-acetoxymethyl-3-ethoxyoxetan-2-yl)methyl acetate (4,4'-di-O-acetyl-1,3-anhydro-2-O-ethyl-DL-apiitol) (37), respectively.
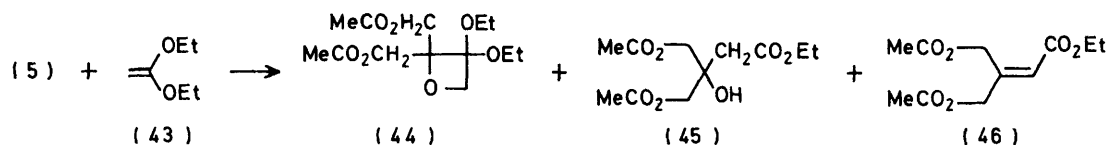
Moreover, the reaction of (5) with 1,1-diethoxyethene

6.50 when C-2 is substituted by an acetoxy-group, at δ 5.29—5.64 when substituted by an alkoxy-group, and at δ 4.49—4.79 when it has no substituent. The protons at the 3-position of the oxetan ring * appeared at δ 5.29—5.59 when C-3 is substituted by an acetoxy-group, at δ 4.2—4.8 when substituted by an alkoxy-group, and at δ 2.54—2.93 when it has no substituents. The methylene protons of the acetoxymethyl group, by and large, appeared as an AB quartet due to the hindrance on their free rotation. The difference in the chemical shift of the

	R^1	R^2	R^3
(23)	OCOMe,	OCOMe,	H
(24)	OCOMe,	H,	OCOMe
(25)	OCH$_2$Ph,	OCOMe,	H
(26)	OCH$_2$Ph,	H,	OCOMe
(27)	OCH$_2$CH$_2$O		H
(28)	H,	OCOMe,	H
(29)	H,	OCOMe,	Me
(30)	H,	OEt,	H

	R^1	R^2	R^3
(31)	OCOMe,	OCOMe,	H (cis)
(32)	OCOMe,	OCOMe,	H (trans)
(33)	OCH$_2$Ph,	OCOMe,	H
(34)	OCH$_2$CH$_2$O,		H
(35)	H,	OCOMe,	H
(36)	H,	OCOMe,	Me
(37)	H	OEt	H

	R^1	R^2	R^3
(38)	OCH$_2$Ph,	OCOMe,	H
(39)	H,	OCOMe,	H
(40)	H,	OEt,	OEt

(41)

(42)

(43) gave (2-acetoxymethyl-3,3-diethoxyoxetan-2-yl)-methyl acetate (44) and ethyl 4-acetoxy-3-acetoxy-methyl-3-hydroxybutyrate (45). The formation of (45) was also observed in the reaction performed in the dark; the reaction in benzene under reflux gave (45) and ethyl 4-acetoxy-3-(acetoxymethyl)crotonate (46) (cf. Table 5). The compounds (45) and (46) might be obtained via oxetan (40); oxetan formation from keten acetals and

gem protons of (31) and (32), i.e. 0.06 and 0.20, and 0.27 and 0.15, respectively, is assumed to arise from the steric hindrance by the acetoxy-group on the ring to the rotation of the acetoxymethyl group. Therefore, the stereochemistry of (31) and (32) was concluded to be cis and trans, respectively. Each of the two isomers of (33) and (38) we were unable to isolate in a pure form. However, by inspection of the ^{1}H n.m.r. spectra of frac-

carbonyl compounds in the dark has already been reported.[13]

The structural determination of the products was accomplished through ^{1}H n.m.r. spectroscopy (see Table 3) and i.r. spectroscopy. The oxetan structure was assigned on the basis of the chemical shift of the oxetan ring-protons and their splitting pattern. The protons at the 2-position of the oxetan ring * appeared at δ 6.24—

tions from column chromatography, the formation of the four isomers was confirmed, and their structures were determined. Ring-fusion in (34) is presumably cis judging from the spectral pattern of methylene proton signals in the dioxan moiety, i.e. three of them appeared

* These are different from the locants given in Table 3; the 2- and 3-position correspond to the 1- and 2-position given in Table 3, respectively (see footnote a in Table 3).

at δ 3.5—4.1 and one of them at δ 4.1—4.6 as a multiplet; the assignment was based on an analysis by the INDOR technique, and this pattern is in good agreement with those of the compounds having homologous ring structures.[14] The structures of (35), (39), (36), (37), and (44) were determined by comparing the chemical shift of their H-1 and H-2 protons (see Table 3). The structure of (41) was determined on the basis of its [1]H n.m.r. spectrum (see Experimental section), *i.e.* four *O*-acetyl methyl signals, three 1-proton signals at δ 6.48, 4.45, and 4.20 which are coupled to each other, a 1-proton

TABLE 5

Reactions of 1,3-diacetoxypropan-2-one (5) with
1,1-diethoxyethene (43) [a]

		Yield (%)			
		Products			
Entry	Time/ h	(44)	(45)	(46)	(5)
1	30 [b]	35	17		47
2	50 [b]	48	19	Trace	27
3	30 [c]		6		92
4	50 [c]		7		87
5	50 [d]		20	24	54

[a] All the reactions were performed using (5) (0.25M) and (43) (0.5M) in benzene. [b] These reactions were performed under photoirradiation. [c] These reactions were performed in the dark. [d] The reaction was performed under reflux without replacing the atmosphere with argon.

broad singlet at δ 7.06, and a 2-proton broad singlet at δ 4.57. This product was presumably formed from the biradical intermediate (42) which is also the intermediate in the formation of (31) and (32). Compound (24) was identical with that reported in the literature [15] on the basis of its i.r. and [1]H n.m.r. spectral data (see Experimental section). The structure of (45) was assigned on the basis of its i.r. spectrum, which showed the specific absorption band for a hydroxy-group, and the [1]H n.m.r. spectrum, showing proton signals of one ethoxy-group and two equivalent acetoxymethyl substituents. The structure of (46) was also determined on the basis of spectral data, *i.e.* i.r. absorption bands at 1 750, 1 720, and 1 660 cm^{-1}, and [1]H n.m.r. signals due to a 1-proton quintet at δ 6.01 and two 2-proton signals at δ 5.29 and 4.76, with both of which the 1-proton quintet couples with a small *J*-value. The regioisomer of (37) was not isolated, and it might have been hydrolysed on the silica gel column; 2-alkoxyoxetans are generally accepted to be susceptible to hydrolysis,[16] and similarly, (33) and (34) were gradually hydrolysed on standing in contact with the atmosphere. Moreover, the regioisomer of (44), *i.e.* (40), is assumed to be much more susceptible to hydrolysis, and was therefore transformed into (45) and then to (46) at elevated temperatures. In these photochemical reactions, furthermore, all the starting alkenes other than vinyl acetate (28) survived even after the reaction.

As in ordinary oxetan formation reactions,[3,4] the photocycloaddition reactions described herein may proceed through excited (5) or (21) in the n→π* triplet state. Addition of a typical triplet-state quencher, penta-2,4-diene, to the reaction system, however, did not

confirm the assumption, but instead the quencher reacted with compound (5). An attempt to use biphenyl (E_T 65.7 kcal mol^{-1}) [17] in place of penta-2,4-diene (Table 2, Entry 15) was also found not to affect the oxetan formation. This aspect of the reaction is thus impossible to discuss unambiguously, due to the difficulty in selecting a potential quencher.

EXPERIMENTAL

The following instruments were used: i.r., Hitachi 285; [1]H n.m.r., Varian T–60, EM–360, and EM–390; the spectra were recorded with a T–60 instrument for solutions in CDCl$_3$ containing tetram(.hylsilane unless otherwise stated; g.l.c., Hitachi K–53 [1-m column of 10% SE 30 on Chromosorb W (60—80 mesh)]; carrier gas, nitrogen; detection by use of FID); m.p., Yanagimoto Micro Melting Point Apparatus (mainly) or a Büchi Schmeltzpunktbestimmungsapparat [(indicated with m.p. (Büchi)].

Column chromatographic separations on silica gel were performed by use of Wakogel C–300 (Wako Pure Chemicals, Japan), and t.l.c. was performed on DC–Alufolien Kieselgel 60 F254 (thickness 0.2 mm).

Photoirradiation of a mixture was performed by means of a Ushio 450-W high-pressure mercury lamp in a Pyrex glass test tube at room temperature with a distance of *ca.* 5 cm, after passing argon gas through the mixture. All the solvents used for the photoirradiation were purified as usual. The resulting mixtures were evaporated below 35 °C, and all evaporation was performed using a suction pump.

Microanalyses were performed by the Laboratory of Organic Analysis, Department of Chemistry, Tokyo Institute of Technology.

Vinyl acetate (28), isopropenyl acetate (29), and ethoxyethene (30) were purchased commercially, and the former two were purified by distillation prior to use. 1,3-Diacetoxypropan-2-one (5),[18] 1,3-dioxol-2-one (6),[19] diethyl mesoxalate (21),[20] 2,3-dihydro-1,4-dioxin (27),[21] and 1,1-diethoxyethene (43) [22] were prepared according to known methods. We developed a novel synthetic method for 1,3-dimethoxypropan-2-one (8) and 1,3-bis(benzyloxy)propan-2-one (13) (see later), since the known method [23] gives low yields, and there is difficulty in separating product from starting materials. 2,2-Dimethyl-1,3-dioxan-5-one (20) was prepared according to the method [24] used for the synthesis of an analogue (see later). The mixture of (*Z*)- (25) and (*E*)-2-(benzyloxy)vinyl acetate (26) was prepared from 3-(benzyloxy)propane-1,2-diol [25] (see later). (*Z*)-Vinylene diacetate (23) [26] has only previously been known as a by-product. Therefore, we set out to develop a novel synthetic procedure for (23), starting from but-2-ene-1,4-diyl diacetate *via* formylmethyl acetate (details will be reported elsewhere).[27]

Photochemical Reaction of 1,3-*Diacetoxypropan-2-one* (5) *with* 1,3-*Dioxol-2-one* (6).—(a) *Reaction without solvent.* (*cf.* Entry 1, Table 1). Two aliquots of a mixture prepared from (5) (1 045 mg, 6.00 mmol) and (6) (1 033 mg, 12.0 mmol) (liquefied on admixture) were placed between the walls of two double-walled test tubes. The tubes were irradiated for 26 h, after replacing the atmosphere in the tubes with argon gas by four times freezing, evacuating with a water-pump, fusion, and introduction of argon gas. The resulting gelatinous mass was dissolved in acetone and the solution diluted with benzene. The diluted solution was passed through a short column of silica gel to remove insoluble

materials. The effluent was evaporated and the residue was chromatographed on a column of silica gel (100 ml) using benzene–acetone; this gave (5) (594 mg , 58% recovery yield) and (7-acetoxymethyl-3-oxo-2,4,6-trioxabicyclo-[3.2.0]-heptan-7-yl)methyl acetate (7) (358 mg, 23% yield).

(b) *Reaction in benzene.* (Entry 13, Table 2). Five aliquots of a solution of (5) (871 mg, 5.00 mmol) and (6) (2 153 mg, 25.0 mmol) in benzene (50 ml) were put into test-tubes, and photoirradiated for 30 h. Column chromatographic separation of the resulting mixture as above after evaporation gave (2-oxo-5-phenyl-1,3-dioxolan-4-yl)methyl acetate (19) (52 mg, 2% yield), (5) (281 mg, 32% recovery yield), and (7) (709 mg, 55% yield).

Compound (7) had m.p. 72—73 °C (from chloroform–diethyl ether); $\nu_{C=O}$(KBr) 1 755 (acetate) and 1 825 cm^{-1} (cyclic carbonate); δ_H see Table 3 (Found: C, 46.05; H, 4.7. $C_{10}H_{12}O_8$ requires C, 46.16; H, 4.65%).

Compound (19) was a syrup; $\nu_{C=O}$ (NaCl) 1 745 (acetate) and 1 805 cm^{-1} (cyclic carbonate); δ_H* 7.42 (5 H, s, Ph), 5.44 (1 H, d, $J_{4,5}$ 6.5 Hz, H-5), 4.74 (1 H, ddd, $J_{4,\alpha}$ 3.0 Hz, $J_{4,\alpha'}$ 4.5 Hz, H-4), 4.45 (1 H, dd, $J_{\alpha,\alpha'}$ 13.0 Hz, H-α), 4.38 (1 H, dd, H-α'), and 2.14 (3 H, s, OCOMe) (Found: C, 60.95; H, 5.2. $C_{12}H_{12}O_5$ requires C, 61.01; H, 5.12%).

Hydrolysis of (7).—A solution of (7) (781 mg, 3.00 mmol) in methanol (40 ml) was stirred for 30 min after the addition of water (40 ml) and Amberlite IRA—400 (OH$^-$) (9 ml); t.l.c. of the resulting solution gave a single spot. The resin was filtered off and was washed with distilled water. The filtrate and the washings were combined and evaporated to a syrup [406 mg, 90% yield as DL-apiose (4)]; this syrup gave a single spot on t.l.c. with five different solvent systems. The syrup was, as usual,[28] converted into 3-C-(hydroxymethyl)-tetrose phenylosazone (apiose phenylosazone) [453 mg, 46% yield from (7)], m.p. 155.5—157 °C (from ethanol) [lit.,[8] m.p. 156—157 °C (from ethanol)] (Found: C, 62.1; H, 6.1; N, 17.3. Calc. for $C_{17}H_{20}N_4O_3$: C, 62.18; H, 6.14; N, 17.06%). R_F Values of (4) on t.l.c. were 0.23 [solvent system chloroform–methanol–acetic acid (20 : 8 : 1 v/v)], 0.49 [butanol–pyridine–water (14 : 3 : 3 v/v)], 0.45 [butanol–water–acetic acid (3 : 1 : 1 v/v)], 0.52 [propanol–ethyl acetate–water (3 : 2 : 1 v/v)], and 0.56 [butanol–acetone–water (4 : 5 : 1 v/v)].

1,3-Dimethoxypropan-2-one (8).—To a solution of 3,3-bis(hydroxymethyl)-1-oxa-4-azaspiro[4.5]decane [29] (50 g, 0.25 mol) in NN-dimethylformamide (DMF) (1 000 ml), sodium hydride (6 g, 0.26 mol) was added with ice-cooling, and, after 1 h, methyl iodide (15.5 ml, 35.2 g, 0.25 mol) was added dropwise during 30 min. More sodium hydride (6 g, 0.26 mol) was added after 1 h, and then methyl iodide (23.5 ml, 53.4 g, 0.38 mol) was again added dropwise during 30 min. After 2 h, methanol (3 ml) was added to the resulting mixture, and then diethyl ether (1 000 ml). The precipitated sodium iodide was filtered off, and the filtrate was distilled under reduced pressure after evaporation of diethyl ether. The residue was dissolved in chloroform (200 ml), and the resulting solution was washed with water (2 × 200 ml); drying the organic layer over anhydrous magnesium sulphate and evaporation afforded an oil (61 g). The oil was dissolved in 3M hydrochloric acid (200 ml), and the solution was heated at 50 °C for 5 h; a brown oil formed. To the resulting mixture was added solid sodium carbonate (ca. 20 g) until the evolution of carbon dioxide gas ceased. The oily layer was extracted with chloroform (3 × 100 ml).

* Locants used here correspond to those indicated in the structure of (19) in the text.

The aqueous layer was diluted with water to 1 l, and then treated with sodium metaperiodate (56 g, 0.26 mol) below 20 °C. The resulting mixture, after 2 h, was extracted with chloroform (6 × 300 ml), and the organic layer was dried over anhydrous magnesium sulphate. After evaporation, the residue was distilled under reduced pressure to give (8) (13.9 g, 47% yield), b.p. 85.5—86 °C at 32 mmHg [lit.,[23] b.p. 71—71.5 °C at 16 mmHg]; $\nu_{C=O}$(NaCl) 1 730 cm^{-1}; δ_H 4.18 (4 H, s, 2 × CH_2) and 3.43 (6 H, s, 2 × Me) (Found: C, 51.0; H, 8.5. Calc. for $C_5H_{10}O_3$: C, 50.83; H, 8.53%).

Photochemical Reaction of (8) *with* (6).—Eight aliquots of a solution of (8) (2 364 mg, 20.0 mmol) and (6) (3.44 g, 40.0 mmol) in benzene (80 ml) were photoirradiated for 10 h. T.l.c. of the resulting mixture gave no spot due to starting material (8). During the reaction, there appeared a syrupy precipitate and a small amount of crystals on the wall of each test-tube. After removal of the solution by decantation, the syrupy residue was dissolved in methanol, and the resulting crystals of *cis-transoid-cis*-3,5,8,10-tetraoxa-tricyclo[5.3.0.0^{2,6}]decane-4,9-dione (12) (22 mg) were filtered off. Compound (12) was identical with an authentic specimen prepared by the known method [9] (i.r. spectroscopy and m.p.). The benzene solution obtained by decantation was evaporated to a syrup (768 mg), which was then chromatographed on a column of silica gel (120 ml) using benzene–cyclohexane–acetone and benzene–propan-2-ol, giving a mixture which contained crystalline 4-acetyl-5-phenyl-1,3-dioxolan-2-one (11) (15 mg) and 2,4,6-trioxa-bicyclo[3.2.0]heptan-3-one (10) (8 mg), (12) (6 mg), and a mixture containing 3-(methoxymethyl)oxetan-3-ol (9) (430 mg). Recrystallization of the mixture containing (11) from benzene–hexane gave a pure sample of (11) (4 mg). For the mixture containing (9), chromatographic separation of (9) was attempted on a column of silica gel using chloroform–methanol, but resulted only in the isolation of a mixture which is composed mainly of (9) (244 mg); further purification was unsuccessful.

Compound (12) had m.p. (Büchi) >300 °C [lit.,[9] m.p. 320 °C (from acetonitrile)]. *Compound* (11) had m.p. (Büchi) 97.5—100.5 °C (from benzene–hexane); $\nu_{C=O}$(KBr) 1 800 (carbonate) and 1 720 cm^{-1} (ketone); δ_H 7.42 (5 H, s, Ph), 5.68 (1 H, d, J 6.0 Hz, H-5), 4.76 (1 H, d, H-4), and 2.43 (3 H, s, Me) (Found: C, 64.25; H, 5.0. $C_{11}H_{10}O_4$ requires C, 64.07; H, 4.89%).

Compound (10) had m.p. 89—90 °C (from benzene–hexane); $\nu_{C=O}$(KBr) 1 800 cm^{-1} (broad, carbonate); δ_H 6.30 (1 H, d, $J_{1,5}$ 3.5 Hz, H-5), 5.45 (1 H, ddd, $J_{1,7}$ 4.0 Hz, $J_{1,7'}$ 3.0 Hz, H-1), 4.97 (1 H, dd, $J_{7,7'}$ 8.0 Hz, H-7), and 4.75 (1 H, dd, H-7') (Found: C, 41.7; H, 3.45. $C_4H_4O_4$ requires C, 41.39; H, 3.47%). *Compound* (9) was a syrup; δ_H 4.64 (2 H, d, J 6.5 Hz, H-2 and H-4), 4.48 (2 H, d, H-2' and H-4'), 3.68 (2 H, s, CH_2OMe), and 3.45 (3 H, s, Me).

Photochemical Reaction of (8).—Twenty-nine aliquots of a solution of (8) (8.56 g, 72.4 mmol) in benzene (290 ml) were similarly photoirradiated for 10 h; almost all the (8) was found to be consumed (t.l.c.), affording syrupy precipitates at the bottom of each test-tube. The benzene solutions were collected together by decantation from each test-tube, and evaporated. The residue was distilled under reduced pressure to give a mixture of starting material (8) and (9) (13 : 87, by ^{1}H n.m.r. spectroscopy, equivalent to 2% and 13% yield, respectively, based on the weight of the mixture, i.e., 1.3 g); b.p. 77—85 °C at 12 mmHg (Found: C, 51.1; H, 8.45. $C_5H_{10}O_3$ requires C, 50.83; H, 8.53%).

1,3-Bis(benzyloxy)propan-2-one (13).—Sodium hydride

(9.6 g, 0.40 mol) was added to a solution of 3,3-bis(hydroxymethyl)-1-oxa-4-azaspiro[4.5]decane [29] (30 g, 0.15 mol) in DMF (1 000 ml) under ice-cooling with stirring, to which was next added benzyl chloride (50 ml; 55 g, 0.43 mol) during 30 min. In order to quench the excess of sodium hydride, methanol was added to the resulting mixture after 5 h, and then diethyl ether (1 000 ml) was added. The resulting precipitate was filtered off, the filtrate was evaporated, and then DMF removed by distillation under reduced pressure. The residue was dissolved in benzene (200 ml), and the solution was washed with water (2 × 200 ml). Evaporation of the solution, followed by the addition of 3M hydrochloric acid (200 ml), afforded a crystalline precipitate, which, on heating at 60 °C, turned into an oil and separated from the aqueous layer. The mixture was stirred for 2 h, and then cooled with ice–water; solid sodium hydrogencarbonate was then added until evolution of carbon dioxide ceased. The mixture was extracted with chloroform (2 × 200 ml), and dried over anhydrous sodium sulphate. After evaporation of the solvent, the residue was crystallized by addition of benzene to give 1,1-*bis(benzyloxymethyl)-2-hydroxyethylammonium chloride* (45 g, 89% yield); m.p. 131.5—133 °C (Found: C, 64.05; H, 7.05; N, 4.0. $C_{18}H_{23}NO_3$·HCl requires C, 63.99; H, 7.16; N, 4.15%).

The chloride (36 g, 0.11 mol) was then dissolved in water (500 ml), sodium hydroxide (2 g, 0.05 mol) was added, and then sodium metaperiodate (24 g) was added in portions with stirring during 2 h. The resulting mixture was extracted with benzene (500 ml) and the organic layer was washed with water (2 × 500 ml). After drying over anhydrous magnesium sulphate, the benzene solution was evaporated to dryness to yield crystals of (13) (27 g, 94% yield). Recrystallization from ethanol (10 ml) afforded a pure sample (21 g, 74% yield); m.p. 38.5—39 °C;* $\nu_{C=O}$ (KBr) 1 740 cm^{-1}; δ_H 7.31 (10 H, s, 2 × Ph), 4.57 (4 H, s, PhCH$_2$ × 2), and 4.23 (4 H, s, CH$_2$COCH$_2$) (Found: C, 75.65; H, 6.7. $C_{17}H_{18}O_3$ requires C, 75.53; H, 6.71%).

Photochemical Reaction of (13) *with* (6).—Two aliquots of a solution of (13) (1 351 mg, 5.00 mmol) and (6) (860 mg, 10.0 mmol) in benzene (20 ml) were photoirradiated for 30 h. The resulting mixture was evaporated and the residue was chromatographed on a column of silica gel (70 ml) using benzene–cyclohexane–acetone, and benzene–acetone. Thus, were obtained a mixture of (6) and *trans*-7-phenyl-2,4,6-trioxabicyclo[3.2.0]heptan-3-one (14) (329 mg, fraction 1), (14) and 1-benzyloxypropan-2-one (16) (153 mg; fraction 2), (16) and (13) (106 mg; fraction 3), (13) and *cis*-7-phenyl-2,4,6-trioxabicyclo[3.2.0]heptan-3-one (15) (95 mg; fraction 4), 3-benzyloxymethyl-2-phenyloxetan-3-ol (17) and other products (155 mg; fraction 5), a mixture (131 mg; fraction 6), and 1,2-diphenylethane-1,2-diol (18) and other products (202 mg; fraction 7).

Fraction 1, after concentration by use of a high-vacuum pump, was chromatographed again on a column of silica gel by using cyclohexane–acetone to give (14) (275 mg). Fractions 2 and 3 were combined and rechromatographed on a silica gel column by using benzene–acetone, affording (14) (38 mg), (16) (126 mg), an unidentified compound [25 mg; containing 15% of (13)], and (13) (3 mg). Rechromatography of fraction 4 on a column of silica gel using cyclohexane–propan-2-ol afforded (13) (62 mg, containing a small amount of impurity) and (15) (27 mg). Re-chromatography of fraction 5 using benzene–cyclo-

* This compound was not obtained in crystalline form by the previously reported method.[23]

hexane–acetone gave a mixture containing (17) (8 mg) (17) (32 mg), and another mixture containing (17) (5 mg). Separation of fraction 6 by the same method was unsuccessful. For fraction 7, crystallization was induced by the addition of benzene to give (18) (*meso*-isomer) (19 mg). To summarize the compounds isolated above; (14) (313 mg, 16% yield), (16) (126 mg, 15% yield), (13) (69 mg, 5% recovery yield), (15) (27 mg, 1% yield), (17) (32 mg, 2% yield), and (18) (19 mg, 2% yield). Compound (16) was identified with an authentic specimen prepared according to a known method [10] by means of i.r. and ^{1}H n.m.r. spectroscopy.

Compound (14) had m.p. 71—72 °C (from benzene–hexane); $\nu_{C=O}$(KBr) 1 815 cm^{-1}; δ_H 7.40 (5 H, s, Ph), 6.42 (1 H, d, $J_{1,7}$ 4.0 Hz, H-7), 5.79 (1 H, d, $J_{1,5}$ 2.5 Hz, H-5), and 5.11 (1 H, dd, H-1) (Found: C, 62.4; H, 4.15. $C_{10}H_8O_4$ requires C, 62.50; H, 4.20%).

Compound (15) had m.p. 104—105 °C (from methanol); $\nu_{C=O}$(KBr) 1 805 cm^{-1}; δ_H 7.38 (5 H, s, Ph), 6.33 (1 H, d, $J_{1,7}$ 3.5 Hz, H-7), 6.06 (1 H, d, $J_{1,5}$ 4.5 Hz, H-5), and 5.52 (1 H, dd, H-1) (Found: C, 62.65; H, 4.25. $C_{10}H_8O_4$ requires C, 62.50; H, 4.20%).

Compound (16) was a syrup, and had $\nu_{C=O}$ (NaCl) 1 730 cm^{-1}; δ_H 7.32 (5 H, s, Ph), 4.59 (2 H, s, CH$_2$Ph), 4.03 (2 H, s, CH$_2$Ac), and 2.15 (3 H, s, Me).

Compound (17) was a syrup, and had ν_{O-H} (NaCl) 3 400 cm^{-1}; δ_H 7.38 (5 H, s, Ph), 7.35 (5 H, s, Ph), 5.67 (1 H, s, H-2), 4.66 (2 H, s, CH$_2$Ph), 4.64 (1 H, d, J_{HCH} 7.5 Hz, HCHOCH$_2$Ph), 4.56 (1 H, d, HCHOCH$_2$Ph), 3.90 (1 H, d, $J_{4,4'}$ 9.5 Hz, H-4), and 3.72 (1 H, d, H-4').

Compound (18) (*meso*-isomer) had m.p. 135—136 °C (from benzene) (lit.,[11] m.p. 137 °C).

2,2-*Dimethyl-1,3-dioxan-5-one* (20).—5-Amino-5-hydroxymethyl-2,2-dimethyl-1,3-dioxan for the preparation of (20) was synthesized according to a known method; [30] [31] 85—90% yield, m.p. 72—73 °C (from methanol–diethyl ether) [lit.,[30] 55 °C (from diethyl ether), lit.,[31] 54.5—55.5 °C (from diethyl ether)]; δ_H (CD$_3$SOCD$_3$) 3.58 (2 H, d, J 10.5 Hz, H-4 and H-6), 3.42 (2 H, d, H-4' and H-6'), 3.37 (2 H, br s, CH$_2$OH), 1.36 (3 H, s, Me), and 1.28 (3 H, s, Me) (Found: C, 52.05; H, 9.35; N, 8.6. $C_7H_{15}NO_3$ requires C, 52.15; H, 9.38; N, 8.69%). The m.p.s reported in the papers were of the hemihydrate, and there have been no data on elemental analysis reported. The hemihydrate was obtained and had m.p. (Büchi) 53.5—54.5 °C (from aqueous methanol–diethyl ether) (Found: C, 49.55; H, 9.21; N, 8.18. $C_7H_{15}NO_3$·$\frac{1}{2}H_2O$ requires C, 49.40; H, 9.48; N, 8.23%).

The 1,3-dioxan derivative (17.5 g, 0.11 mol) thus obtained was dissolved in water (500 ml), and treated with sodium metaperiodate (25 g, 0.12 mol) with stirring; the mixture was kept below 20 °C. After 1 h, the mixture was extracted with dichloromethane (5 × 200 ml), and the organic layer was dried over anhydrous magnesium sulphate. The organic layer was then evaporated and the residue was distilled under reduced pressure to give *compound* (20) (6.3 g, 45% yield), b.p. 65 °C at 23 mmHg; $\nu_{C=O}$ 1 750 cm^{-1}; δ_H 4.16 (4 H, s, CH$_2$ × 2) and ·1.46 (6 H, s, Me × 2) (Found: C, 55.15; H, 7.7. $C_6H_{10}O_3$ requires C, 55.37; H, 7.75%); this compound was susceptible to hydrolysis.

Photochemical Reaction of (20) *with* (6).—Four aliquots of a solution of (20) (1 301 mg, 10.0 mmol) and (6) (1 724 mg, 20.0 mmol) in benzene (40 ml) were photoirradiated. After 6 h reaction, the resulting solution, whose t.l.c. showed no spot of (20), was evaporated. The residue was chromatographed on a column of silica gel (80 ml) using benzene–

acetone and benzene–methanol. However, no products could be isolated.

Photochemical Reaction of Diethyl Mesoxalate (21) [20] *with* (6).—Three aliquots of a solution of (21) (1 307 mg, 7.51 mmol) and (6) (1 290 mg, 15.0 mmol) in benzene (30 ml) were photoirradiated for 6 h, after which t.l.c. of the resulting solution showed substantial consumption of (21). The mixture was evaporated and was further concentrated by use of a high-vacuum pump to remove unchanged (6). The residue was chromatographed on a column of silica gel (60 ml) using benzene–cyclohexane–acetone to yield *diethyl 3-oxo-2,4,6-trioxabicyclo[3.2.0]heptane-7,7-dicarboxylate* (22) (441 mg, 23% yield) as a syrup; $\nu_{C=O}$ (NaCl) 1 745 (ethyl ester) and 1 840 cm^{-1} (cyclic carbonate); δ_H 6.37 (1 H, d, $J_{1,5}$ 3.5 Hz, H-5), 5.77 (1 H, d, H-1), 4.38 (2 H, q, J 7.0 Hz, OCH$_2$), 4.36 (2 H, q, J 7.0 Hz, OCH$_2$) and 1.33 (6 H, t, Me × 2) (Found: C, 46.35; H, 4.65. C$_{10}$H$_{12}$O$_8$ requires C, 46.16; H, 4.65%).

Photochemical Reaction of 1,3-*Diacetoxypropan-2-one* (5) *with* (Z)-*Vinylene Diacetate* (23).—Two aliquots of a solution of (5) (870 mg, 5.00 mmol) and (23) (1 442 mg, 10.0 mmol) in benzene (20 ml) were photoirradiated for 40 h. The resulting mixtures were combined and evaporated, and the residue was chromatographed on a column of silica gel (100 ml) using benzene–cyclohexane–acetone and benzene–acetone. Thus, were obtained a mixture of (E)- and (Z)-vinylene diacetate (24) and (23) [(24) : (23) = 42 : 58, calculated by means of ^{1}H n.m.r. integration] (644 mg), (23) (85 mg), (5) (229 mg), a mixture of (5), 2-(1,2-diacetoxy-ethoxy)propenylene diacetate (41), and *trans*-4,4-bis-(acetoxymethyl)oxetan-2,3-diyl diacetate (32) (40 mg), and a mixture of (32) and its *cis*-isomer (31) [(32) : (31) = 48 : 52] (1 117 mg). The mixture of (5), (41), and (32) (40 mg) was re-chromatographed on a column of silica gel using benzene–acetone, to give (5) (5 mg), (41) (16 mg), and (32) (12 mg). The mixture of (32) and (31) was similarly re-chromatographed using benzene–cyclohexane–acetone to give each pure sample. Thus were obtained (24) (270 mg, 19% yield), (23) (459 mg, 32% yield), (5) (234 mg, 27% recovery yield), (41) (16 mg, 1% yield), (32) (547 mg, 34% yield), and (31) (582 mg, 37% yield).

Compound (31) was a syrup; $\nu_{C=O}$ (NaCl) 1 750 cm^{-1} (broad); ^{1}H n.m.r. data: see Table 3 (Found: C, 49.1; H, 5.6. C$_{13}$H$_{18}$O$_9$ requires C, 49.06; H, 5.70%).

Compound (32) was a syrup; $\nu_{C=O}$ (NaCl) 1 750 cm^{-1} (broad); ^{1}H n.m.r. data: see Table 3 (Found: C, 49.1; H, 5.7. C$_{13}$H$_{18}$O$_9$ requires C, 49.06; H, 5.70%).

Compound (41) was a syrup; $\nu_{C=O}$ (NaCl) 1 740—1 760 cm^{-1}; δ_H 7.06 (1 H, br s, CH=C), 6.48 (1 H, dd, J 4.5 and 5.5 Hz, CH–CH$_2$), 4.57 (2 H, br s, CH$_2$–C=), 4.45 (1 H, dd, J 4.5 Hz, HCH–CH), 4.20 (1 H, dd, HCH–CH), 2.20 (3 H, s, Me), 2.12 (3 H, s, Me), and 2.10 (6 H, s, Me × 2) (Found: C, 49.15; H, 5.7. C$_{13}$H$_{18}$O$_9$ requires C, 49.06; H, 5.70%).

Compound (24) had m.p. 23.5—27 °C (lit.,[15] 23 °C); $\nu_{C=O}$ 1 760 cm^{-1}, no absorption bands were observed between 1 600 and 1 700 cm^{-1}; δ_H 7.47 (2 H, s, CH × 2), 2.16 (6 H, s, Me × 2) [δ_H (CCl$_4$) 7.41 and 2.12 (lit.,[15] δ_H 7.33 and 2.10)].

(Z)- (25) *and* (E)-2-(*Benzyloxy*)*vinyl acetate* (26).—To a solution of 3-benzyloxypropane-1,2-diol [25] (73 g, 0.41 mol) in water (1 000 ml) (not completely dissolved), sodium meta-periodate (90 g, 0.42 mol) was added with stirring below 20 °C, and the resulting mixture was extracted with ethyl acetate (6 × 500 ml), after 1 h stirring. The organic layer was dried over anhydrous magnesium sulphate, and evapor-

ated to a syrup (62 g). The residue was mixed with sodium acetate (1 g, 0.012 mol) and acetic anhydride (100 ml), and the mixture was refluxed for 30 min. After cooling, the mixture was poured into a saturated solution of sodium hydrogencarbonate in water (1 500 ml) with stirring. After 1 h, the resulting mixture was extracted with chloroform (1 000 ml) and the organic layer was washed with water (2 × 500 ml). After drying over anhydrous magnesium sulphate, the solution was evaporated to remove the solvent and acetic anhydride, and then distilled at 2 mmHg. Thus were obtained the first fraction (28 g; b.p. 139—148 °C) as a 56 : 12 : 32 mixture of (25), (26), and 2-(benzyloxy)-ethylidene diacetate (47) (the proportion was obtained by ^{1}H n.m.r. spectroscopy), and the second fraction (12 g; b.p. 148—165 °C) as a 15 : 10 : 75 mixture of (25), (26), and (47). Crystallization of the distillation residue gave 5-benzyloxy-2,6-bis(benzyloxymethyl)-1,3-dioxan-4-yl acetate (48) (6.9 g, 10% yield). Compounds (25), (26), and (47) were obtained in a total yield of 17.5 g (23% yield), 4.5 g (6% yield), and 18 g (18% yield), respectively. Re-distillation of the first fraction gave a pale yellow mixture of (25), (26), and (47) (77 : 12 : 11) (74.5 g; b.p. 107—110 °C at 0.6 mmHg), a part of which was chromatographed on a column of silica gel using hexane–acetone to give a colourless mixture of (25) and (26) (92 : 8). This mixture was used for the photochemical reaction. Re-chromatography of the mixture yielded pure (25), and the structure of (26) was confirmed by isolating it in a photochemical reaction which will be described later.

Compound (25) was a syrup; $\nu_{C=O}$ (NaCl) 1 755 cm^{-1} and $\nu_{C=C}$ 1 690 cm^{-1}; δ_H 7.33 (5 H, s, Ph), 6.51 (1 H, d, J 3.5 Hz, CH), 5.69 (1 H, d, CH), 4.87 (2 H, s, CH$_2$), and 2.15 (3 H, s, OCOMe) (Found: C, 68.65; H, 6.2, and the 92 : 8 mixture gave C, 68.75; H, 6.35. C$_{11}$H$_{12}$O$_3$ requires C, 68.73; H, 6.29%).

Compound (47) was a syrup; δ_H 7.31 (5 H, s, Ph), 6.96 (1 H, t, J 5.0 Hz, CH), 4.61 (2 H, s, PhCH$_2$), 3.66 (2 H, d, CHCH$_2$O), and 2.08 (6 H, s, OCOMe × 2).

Compound (48) had m.p. 100—101 °C (from methanol); $\nu_{C=O}$ (KBr) 1 760 cm^{-1}; δ_H 7.29 (15 H, s, Ph × 3), 7.16 (1 H, br d, J 7.0 Hz, H-4), 4.93 (1 H, t, J 4.5 Hz, H-2), 4.58 (6 H, s, PhCH$_2$ × 3), 3.5—3.9 (6 H, m), and 2.04 (3 H, s, COMe) (Found: C, 70.65; H, 6.6. C$_{29}$H$_{32}$O$_7$ requires C, 70.71; H, 6.55%).

Photochemical Reaction of (5) *with* (25), (26).—Two aliquots of a solution of (5) (871 mg, 5.00 mmol) and (25), (26) (92 : 8) (1 923 mg, 10.0 mmol) in benzene (20 ml) were similarly photoirradiated for 30 h. After the reaction, the resulting mixture was concentrated *in vacuo* and the residue was chromatographed on a column of silica gel (120 ml) using benzene–cyclohexane–acetone and benzene–acetone. Thus were obtained (26) (222 mg), a 56 : 44 mixture of (25) and (26) (342 mg), (25) (551 mg), a mixture of (5), 2,2-bis(ace-toxymethyl)-4-(benzyloxy)oxetan-3-yl acetate (33a), (33b), and 4,4-bis(acetoxymethyl)-3-(benzyloxy)oxetan-2-yl acetate (38a), (38b) (391 mg; fraction 4), a mixture of (5), (33), and (38) (664 mg; fraction 5), and a 42 : 24 : 34 mixture of (33b), (38a), and (38b) (342 mg). Re-chromatography of fractions 4 and 5 on a column of silica gel (70 ml) using cyclohexane–propan-2-ol gave (33a) (108 mg; containing impurity), a mixture of (33) and (38a) [291 mg; (33a) : (33b) : (38a) = 33 : 59 : 8], a mixture of (33b) and (38) [305 mg; (33b) : (38a) : (38b) = 52 : 30 : 18], and (5) (329 mg, 38% recovery yield) (proportions calculated by means of ^{1}H n.m.r. spectroscopy). Thus the compounds obtained were as follows:

(26) (372 mg, 19% yield), (25) (743 mg, 39% yield), (33a) (204 mg, 11% yield, containing impurity), (33b) (474 mg, 26% yield; containing impurity), (38a) (197 mg, 11% yield; containing impurity), (38b) (171 mg, 9% yield), and (5) (329 mg, 38% recovery yield).

Compound (26) was a syrup; $\nu_{C=O}$ (NaCl) 1 750 cm^{-1} and $\nu_{C=C}$ 1 670 cm^{-1}; δ_H 7.32 (5 H, s, Ph), 7.11 (1 H, d, *J* 11.0 Hz, CH), 6.78 (1 H, d, CH), 4.71 (2 H, s, CH_2Ph), and 2.08 (3 H, s, OCOMe) (Found: C, 68.6; H, 6.35. $C_{11}H_{12}O_3$ requires C, 68.73; H, 6.29%).

Compounds (33) and (38); ^{1}H n.m.r. data, see Table 3 [Found: C, 58.8; H, 6.0 for a mixture of (33b), (38a), and (38b). $C_{18}H_{22}O_8$ requires C, 59.01; H, 6.05%].

Photochemical Reaction of (5) *with* 2,3-*Dihydro*-1,4-*dioxin* (27).—Two aliquots of a solution of (5) (870 mg, 5.00 mmol) and (27) (862 mg, 10.0 mmol) in benzene (20 ml) were photoirradiated in the same way as above for 30 h. The i.r. spectrum of the resulting mixture showed $\nu_{C=C}$ at 1 650 cm^{-1}, due to unchanged (27). The mixture was evaporated and the residue was chromatographed on a column of silica gel (70 ml) using benzene–acetone to give (5) (418 mg) a 12 : 88 mixture of (5) and (8-acetoxymethyl-2,5,7-trioxabicyclo-[4.2.0]octan-8-yl)methyl acetate (34) (51 mg), and (34) (285 mg) [proportions of (5) and (34) in the mixture calculated by means of ^{1}H n.m.r. spectroscopy]. Thus, were obtained (5) (424 mg, 49% yield), and (34) (320 mg, 25% yield).

Compound (34) had m.p. 65—65.5 °C (from benzene-hexane); $\nu_{C=O}$ (KBr) 1 740 cm^{-1}; ^{1}H n.m.r. data, see Table 3 (Found: C, 50.9; H, 6.15. $C_{11}H_{16}O_7$ requires C, 50.77; H, 6.20%).

Photochemical Reaction of (5) *with Vinyl Acetate* (28).—Three aliquots of a solution of (5) (1 306 mg, 7.50 mmol) and (28) (1.30 g, 15.0 mmol) in benzene (30 ml) were photoirradiated in the same way as above; g.l.c. showed consumption of >90% (28) after irradiating for 15 h. The resulting mixture was evaporated and the residue was chromatographed on a column of silica gel (80 ml) using benzene–acetone to give (5) (708 mg, 54% recovery yield), 2,2-bis-(acetoxymethyl)oxetan-3-yl acetate (35) (134 mg), a 65 : 35 mixture of (35) and 4,4-bis(acetoxymethyl)oxetan-2-yl acetate (39) (244 mg) and (39) (33 mg). On the whole, were obtained (35) (292 mg, 15% yield) and (39) (118 mg, 6% yield). The mixture of (35) and (39) was further repeatedly chromatographed using cyclohexane–propan-2-ol to give pure samples. Retention time of (28) on g.l.c. was 3.6 min under the conditions used [oven temperature, 60 °C; injection temperature, 130 °C; and carrier gas, nitrogen at 0.4 kg cm^{-2}].

Compound (35) was a syrup; $\nu_{C=O}$ (NaCl) 1 740—1 750 cm^{-1}; ^{1}H n.m.r. data, see Table 3 (Found: C, 50.9; H, 6.25. $C_{11}H_{16}O_7$ requires C, 50.77; H, 6.20%).

Compound (39) was a syrup; $\nu_{C=O}$ (NaCl) 1 745 cm^{-1}; ^{1}H n.m.r. data, see Table 3 (Found: C, 50.7; H, 6.15. $C_{11}H_{16}O_7$ requires C, 50.77; H, 6.20%).

Photochemical Reaction of (5) *with Isopropenyl Acetate* (29). —Five aliquots of a solution of (5) (870 mg, 5.00 mmol) and (29) (2.50 g, 25 mmol) in benzene (50 ml) were photoirradiated for 20 h. After the reaction, the i.r. spectrum of the mixture still showed the absorption band of 1 670 cm^{-1} (C=C) due to (29). The resulting mixture was evaporated and the residue was chromatographed on a column of silica gel (70 ml) using cyclohexane–propan-2-ol, to give 2,2-bis-(acetoxymethyl)-3-methyloxetan-3-yl acetate (36) (750 mg, 55% yield) and (5) (323 mg, 37% recovery yield).

Compound (36) was a syrup; $\nu_{C=O}$ (NaCl) 1 745 cm^{-1}; ^{1}H

n.m.r. data, see Table 3 (Found: C, 52.5; H, 6.85. $C_{12}H_{18}O_7$ requires C, 52.55; H, 6.62%).

Photochemical Reaction of (5) *with Ethoxyethene* (30).—Two aliquots of a solution of (5) (871 mg, 5.00 mmol) and (30) (720 mg, 10.0 mmol) in benzene (20 ml) were similarly photoirradiated for 30 h. G.l.c. of the mixture obtained indicated that >50% of (30) was remained unchanged. After evaporation of the resulting mixture, the residue was chromatographed on a column of silica gel (70 ml) using cyclohexane–propan-2-ol to give (2-acetoxymethyl-3-ethoxyoxetan-2-yl)methyl acetate (37) (587 mg, 48% yield) and (5) (275 mg, 32% recovery yield). Retention time of (30) on g.l.c. was 2.6 min (oven temperature, 60 °C; injection temperature, 130 °C; carrier gas, nitrogen at 0.4 kg cm^{-2}).

Compound (37) was a syrup; $\nu_{C=O}$ (NaCl) 1 750 cm^{-1}; ^{1}H n.m.r. data, see Table 3 (Found: C, 53.55; H, 7.5. $C_{11}H_{18}O_6$ requires C, 53.65; H, 7.37%).

Photochemical Reaction of (5) *with* 1,1-*Diethoxyethene* [22] (43).—Two aliquots of a solution of (5) (871 mg, 5.00 mmol) and (43) (1.06 g, 10.0 mmol) in benzene (20 ml) were photoirradiated for 30 h. After the reaction, the resulting solutions were combined and evaporated, and the residue was chromatographed on a column of silica gel (80 ml) using benzene–cyclohexane–acetone to give (2-acetoxymethyl-3,3-diethoxyoxetan-2-yl)methyl acetate (44) (350 mg), a 40 : 60 mixture of (44) and (5) (404 mg; proportions by ^{1}H n.m.r. spectroscopy), (5) (169 mg), and ethyl 4-acetoxy-3-acetoxymethyl-3-hydroxybutyrate (45) (220 mg, 17% yield). Overall were obtained (44) (512 mg, 35% yield) and (5) (411 mg, 47% recovery yield). As a control, another two aliquots were kept in the dark, and treated in the same way as above, giving (45) (78 mg, 6% yield) and (5) (802 mg, 92% recovery yield).

Compound (44) was a syrup; $\nu_{C=O}$ (NaCl) 1 745 cm^{-1}; ^{1}H n.m.r. data, see Table 3 (Found: C, 53.9; H, 7.6. $C_{13}H_{22}O_7$ requires C, 53.78; H, 7.64%).

Compound (45) was a syrup; $\nu_{C=O}$ (NaCl) 1 740 cm^{-1} (br); δ_H 4.23 (2 H, q, *J* 7.0 Hz, CH_2Me), 4.18 (4 H, s, CH$_2$OAc × 2), 2.67 (2 H, s, CH_2CO$_2$Et), 2.12 (6 H, s, MeCO × 2), and 1.30 (3 H, t, *Me*CH$_2$) (Found: C, 50.45; H, 6.9. $C_{11}H_{18}O_7$ requires C, 50.37; H, 6.92%).

Thermal Reaction of (5) *with* (43).—A solution of (5) (870 mg, 5.00 mmol) and (43) (1.16 g, 10.0 mmol) in benzene (20 ml) was refluxed for 50 h. The resulting solution was evaporated and the residue was chromatographed in the same way as above to give ethyl 4-acetoxy-3-acetoxymethyl-crotonate (46) (288 mg, 24% yield), (5) (469 mg, 54% recovery yield), and (45) (268 mg, 20% yield).

Compound (46) was a syrup; $\nu_{C=O}$ (NaCl) 1 750 and 1 720 cm^{-1}, $\nu_{C=C}$ 1 660 cm^{-1}; δ_H 6.01 (1 H, quintet, *J* 1.5 Hz, =CHCO$_2$Et), 5.29 (2 H, br s, CH_2OAc), 4.76 (2 H, br s, CH_2OAc), 4.22 (2 H, q, *J* 7.0 Hz, CH_2Me), 2.14 (3 H, s, COMe), 2.10 (3 H, s, COMe), and 1.31 (3 H, t, *Me*CH$_2$) (Found: C, 53.85; H, 6.6. $C_{11}H_{16}O_6$ requires C, 54.09; H, 6.60%).

REFERENCES

[1] Y. Araki, K. Senna, K. Matsuura, and Y. Ishido, *Carbohydrate Res.*, 1978, **65**, 159.
[2] Preliminary communication: Y. Araki, J. Nagasawa, and Y. Ishido, *Carbohydrate Res.*, 1977, **58**, C4.