Reactions of Unsaturated 1,3-Dioxan Derivatives. Part VI.† Addition of 2-(2-Furyl)-1,3-dioxan and its Derivatives to Maleic Anhydride

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The reaction of 2-(2-furyl)-1,3-dioxan with maleic anhydride in diethyl ether or benzene is stereochemically heterogeneous, yielding a mixture of *endo*- and *exo*-adducts. The structures of these adducts have been studied by means of bromination and lactonization reactions and i.r. and n.m.r. spectroscopy.

It is generally accepted that diene addition reactions are stereochemically non-homogeneous. The steric outcome depends upon the reaction conditions, the *endo*-adduct being formed more rapidly, but being less thermodynamically stable than the *exo*-isomer, which is the predominant product of reaction for prolonged periods or at high temperatures.[1]

The stereochemistry of the reaction of furan with maleic anhydride or maleic acid has been considered in terms of an *endo–exo*-adduct equilibrium.[2] It seemed probable that the introduction of a 1,3-dioxan-2-yl substituent into the furan ring would change the equilibrium situation. Mavoungou-Gomes[3] has reported a brief study of the reactions of 2-(2-furyl)-1,3-dioxolan and 2-(2-furyl)-1,3-dioxan with maleic anhydride in diethyl ether at 0 °C, and proposed, on the basis of n.m.r. analysis, that the products had the *exo*-configuration. The present paper shows that this assumption was incorrect. We have recently reported[4] that 2-(2-furyl)-5,5-dimethyl-1,3-dioxan and maleic anhydride give two stereoisomeric adducts (1 : 1) when the reaction is carried out at 0—20 °C.

In an attempt to investigate the generality of stereo-

† Part V, ref. 4

[1] K. Alder, F. W. Chambers, and W. Trimborn, *Annalen*, 1950, **566**, 27.

[2] J. A. Berson and R. Swidler, *J. Amer. Chem. Soc.*, 1953, **75**, 1721.

[3] L. Mavoungou-Gomes, *Bull. Soc. chim. France*, 1967, 1753.

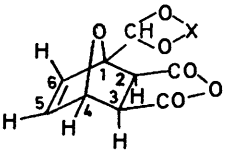
[4] J. Maślińska-Solich and Z. Jedliński, *Bull. Acad. polon. Sci., Ser Sci. chim.*, 1974, **22**, 749.

chemically non-homogeneous 2-(2-furyl)-1,3-dioxan additions to maleic anhydride, some 2-(2-furyl)-1,3-dioxan with various alkyl substituents in the acetal ring have been studied.

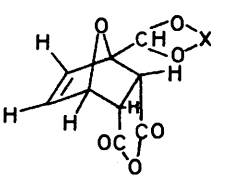
RESULTS AND DISCUSSION

Diels–Alder Addition.—The reaction of 2-(2-furyl)-1,3-dioxans with maleic anhydride was carried out in temperature ranges 0—20 and 60—80 °C in diethyl ether, benzene, or toluene. The products were all 1 : 1 adducts [(1) and (2)], except in the case of 2-(2-furyl)-4-methyl-1,3-dioxan and maleic anhydride, which formed a 1 : 2 adduct at 70 °C. All 2-(2-furyl)-1,3-dioxans react with maleic anhydride to form in the first stage 1 : 1 charge-transfer complexes,[5] as verified by n.m.r. spectroscopy. The complex of 2-(2-furyl)-4-methyl-1,3-dioxan and maleic anhydride undergoes an ' intra-complex ' reaction, yielding a cyclic adduct, with simultaneous complexation of a second molecule of maleic anhydride.[5]

ducts were elucidated on the basis of i.r. and n.m.r. data and chemical transformations.



(1) *exo*



(2) *endo*

a; X = $[CH_2]_3$
b; X = $CHMe{\cdot}[CH_2]_2$
c; X = $CHMe{\cdot}CH_2{\cdot}CHMe$
d; X = $CHMe{\cdot}CH_2{\cdot}CMe_2$
e; X = $[CHMe]_3$
f; X = $CH_2{\cdot}CMe_2{\cdot}CH_2$
g; X = $CH_2{\cdot}CMe_2{\cdot}CHPr^i$
h; X = $CH_2{\cdot}CMeEt{\cdot}CH_2$
i; X = $CH_2{\cdot}CEt_2{\cdot}CH_2$

The i.r. spectra of all adducts showed characteristic anhydride carbonyl absorptions at 1880—1860 and 1780—1795 cm^{-1}, with no apparent difference between *endo*- and *exo*-isomers. In the i.r. spectrum of the adduct (1 g), however, the anhydride carbonyl absorption appears as three peaks at 1865, 1845, and 1785 cm^{-1}, corresponding to two symmetric and one asymmetric stretching vibrations, respectively.

TABLE 1

Chemical shifts (τ) of Diels–Alder addition products

Compound	H-4 (s)	H-5, H-6 (t)	H(2 (d)	H-3 (d)	1,3-Dioxan-2-yl substituent: O·CH·O (s)	OMe	CH·O	Me-*ax*	Me-*eq*	CH	*Me*CH	$J_{2,3}$/Hz
(1a)	4·82	3·6	6·6	6·82	5·12	5·9—6·48				8·5—8·72		6·6
(2a)	4·82	3·6	6·05		5·05	5·7—6·5				8·5—8·72		
(1b)	4·8	3·55	6·62	6·82	5·1	5·9—6·5				8·1—8·6	8·82 (d) 77%; 8·87 (d) 23% at 35 °C; 8·82 (d) 65%; 8·87 (d) 35% at 25 °C	6·95
(2b)	4·6	3·4	5·98		4·87	5·6—6·2				8·1—8·5	8·65 (d) 75%; 8·8 (d) 20%; 8·88 (d) 5% at 25 °C	
(1c)	4·8	3·6	6·6	6·75	5·1		5·9—6·4			8·1—8·5	8·8 (d) 56%; 8·88 (d) 44% at 25 °C	7·05
(2c)	4·75	3·58	5·95		5·0		5·4—6·4			8·1—8·5	8·65 (d) 41%; 8·75 (d) 19%; 8·85 (d) 28%; 8·92 (d) 12% at 25 °C	
(1d)	4·72	3·5	6·55	6·75	4·9		5·9—6·05	8·6	8·72	8·4—8·9	8·86 (d); 8·46 (d)	6·75
(2d)	4·75	3·52	6·075		4·78		5·9—6·2	8·6	8·72	8·4—8·9	8·87 (d); 8·85 (d)	
(1e)	4·6	3·5	6·6	6·8	5·1		5·7—6·1			8·3—9·0	8·7 (d); 8·7 (d); 9·05 (d)	7·1
(2e)	5·52	3·3	5·87		4·77		5·7—6·9			8·3—9·0	8·75 (d); 8·77 (d); 9·0 (d)	
(1g)	4·65	3·38	6·45	6·62	5·0	6·08—6·45		8·84	9·16	8·12 (d)	8·92 (d) 50%; 9·00 (d) 50%	6·75
(1h)	4·75	3·5	6·5	6·75	5·17	6·05—6·5		8·8	9·35	8·2—9·0		7·56
(2h)	4·65	3·47	5·0		5·02; 5·05	6·05—6·5		8·75	9·3	8·2—9·0		
(1i)	4·8	3·57	6·6	6·75	5·22	6·0—6·5				8·2	8·7 (t); 9·4 (t)	7·25
(2i)	4·75	3·45	6·05		5·07	6·1—6·5				8·2	8·8 (t); 9·5 (t)	

Reaction at 0—20 °C in most cases gave two compounds (1a—i) and (2a—f, h, and i), whereas reaction at 60—80 °C gave only one isomer (1). An exception was the reaction of 2-(2-furyl)-6-isopropyl-5,5-dimethyl-1,3-dioxan, which also gave one isomer only at 0—20 °C.

The products obtained at 0—20 °C decompose in air with irreversible destruction of 2-furyl-1,3-dioxans to furfuraldehyde. This is shown by darkening of the products and by the appearance of carbonyl i.r. absorption (1665 cm^{-1}). The pure adducts (1a—i) on the other hand are much more stable, and on hydrolysis of the anhydride ring, yield diacids or carboxy-esters.

Structures of the Adducts.—The structures of the pro-

[5] J. Maślińska-Solich, *Roczniki Chem.*, 1975, **49**, No. 3.

In the n.m.r. spectra of the adducts (1a—i) the H-2 and -3 signals form a simple AB quartet at τ *ca.* 6·75 and *ca.* 6·5 (*J* 6·6—7·65 Hz). The magnitude of the coupling constants suggested that H-2 and -3 have the *endo*-configuration. The *exo*-configuration of H-2 and -3 in the *endo*-adducts (2) would be expected to result in an AB quartet with *J* 10—12 Hz. Chemical shifts and coupling constants are summarized in Table 1.

The n.m.r. spectra of the adducts obtained at 0—20 °C [mixtures of (1) and (2)] exhibited the same signals as the *exo*-isomers (1), along with further signals corresponding

to H-2 and -3 (as doublets) and the O·CH·O (acetal) proton, deshielded by *ca.* 0·65 and 0·1 p.p.m., respectively. This deshielding effect is probably obscured by the anisotropic effects of lone-pair electrons on carbonyl oxygen atoms in the *endo*-isomers. The differences in chemical shift of these protons facilitate quantitative analysis of *endo*-composition in the mixtures of adducts.

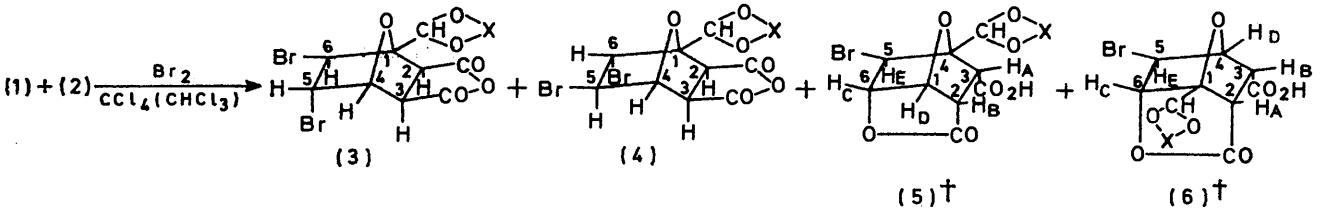
Additional distinctive features in the n.m.r. spectra are the shifts of 4- and 6-methyl protons in the 1,3-dioxan unit. Methyl signals were observed as two separate doublets (1b, c, and g), as four doublets (2c), and as three doublets (2b), J 6·3 Hz, showing temperature-dependent area ratios. These methyl signals at 45 °C coalesce to one doublet in the cases of 2-(2-furyl)-4-methyl-, 2-(2-furyl)-4,6-dimethyl-, and 2-(2-furyl)-6-isopropyl-5,5-dimethyl-1,3-dioxans. This effect disappeared after cleavage of the anhydride ring in the adducts (Table 1). Thus the rotational isomerism of the 4-methyl-, 4,6-dimethyl-, or 6-isopropyl-5,5-dimethyl-1,3-dioxan-2-yl substituent (presumably in a chair or a distorted chair form) is apparently due to steric hindrance by the 5-membered anhydride ring. At elevated temperature the rotation process changes the environment of the 1,3-dioxan-2-yl substituent and thus renders the methyl groups magnetically equivalent.

Steric hindrance of alkyl substituents at C-4 and -6 in the 1,3-dioxan ring in both *endo*- and *exo*-isomers influenced the rate of Diels–Alder addition, and the *endo* : *exo* ratio. The presence of large groups at C-4 and -6 disfavours formation of the *endo*-adduct. In fact, no *endo*-isomer of compound (9) was detected. The order of activity of 2-furyl-1,3-dioxans is as follows: a > f ~ i > h > b > c > d > g > e. The variation of product composition with time (Table 2) unambiguously establishes that the 2-(2-furyl)-5,5-diethyl-1,3-dioxan–maleic anhydride reaction follows the typical kinetic–energetic pattern. *endo*-Addition is a rate-favoured process but the *endo*-adduct is thermodynamically unstable with respect to the *exo*-adduct, which gradually accumulates at the expense of the former.

A repulsive steric interaction between the 1,3-dioxan ring and the *endo*-anhydride ring is probably a cause of the low stability of the *endo*-adducts. In polar solvents such as acetone, chloroform, and pyridine the *endo*-adducts (2a—i) decompose even at ambient temperature (in 2—10 h), regenerating the maleic anhydride and 2-(2-furyl)-1,3-dioxans. This is confirmed by the disappearance of the n.m.r. doublets due to H-2 and -3 (τ *ca.* 6·0) and the appearance of new peaks at τ 2·55, 3·6, and 4·55 (due to H-5, -4, and -3 of the furyl substituent) and a singlet at τ 2·8 (two protons of maleic anhydride). The chemical shifts of the protons of the adducts (1) and (2) and their coupling constants were markedly solvent-dependent. In [^{2}H]chloroform or [$^2H_5$]pyridine, H-2 and -3 of the adducts gave rise to singlets in the range τ 6·75—7·0, instead of two doublets. This effect is not observed in the case of the furan–maleic anhydride adduct, and is believed to be due to a second-order n.m.r. phenomenon, *i.e.* the difference in chemical shifts between H-2 and -3 being of the same order as the coupling constant.

N.m.r. studies of the adducts obtained at 0—20 °C showed no clear correlation between the coupling constants of H-2 and -3 in the *endo*-adducts (Table 1); thus these were of no help in determination of their configuration.

The structures of the adducts were confirmed by a study of their chemical reactions. Attempts to separate the mixtures of *endo*- and *exo*-isomers were unsuccessful.



SCHEME 1 † For convenience, these compound numbers are also used to refer to the corresponding methyl (or ethyl) esters [*cf.* (7) and (8)]

Therefore attempts were made to isolate them as stable derivatives. Since saturation of the olefinic bond of the adducts renders them incapable of reversion to their components, the first attempts involved the direct bromination of the reaction mixture obtained at 0—20 °C. The initial crystalline product which precipitated upon bromination in carbon tetrachloride or chloroform consisted of the crude dibromo-anhydride (4), which was identical with the compound obtained upon bromination of the adduct (1). The mother liquors contained the bromo-lactone acids (5) and (6) (Scheme 1). The structures of these compounds were determined by i.r. and n.m.r. spectroscopy.

TABLE 2

Composition of products of the 5,5-diethyl-2-(2-furyl)-1,3-dioxan–maleic anhydride reaction †

Time (days)	*exo*-Isomer (%)	*endo*-Isomer (%)	Total yield (%)
1	14	86	21·5
2	18	72	38·7
4	35	65	56·2
6	45·9	54·1	96·4

† All runs at 0 °C; reagents: 5,5-diethyl-2-(2-furyl)-1,3-dioxan (0·1 mol) and maleic anhydride (0·1 mol) in diethyl ether (100 ml); compositions estimated by n.m.r. spectroscopy.

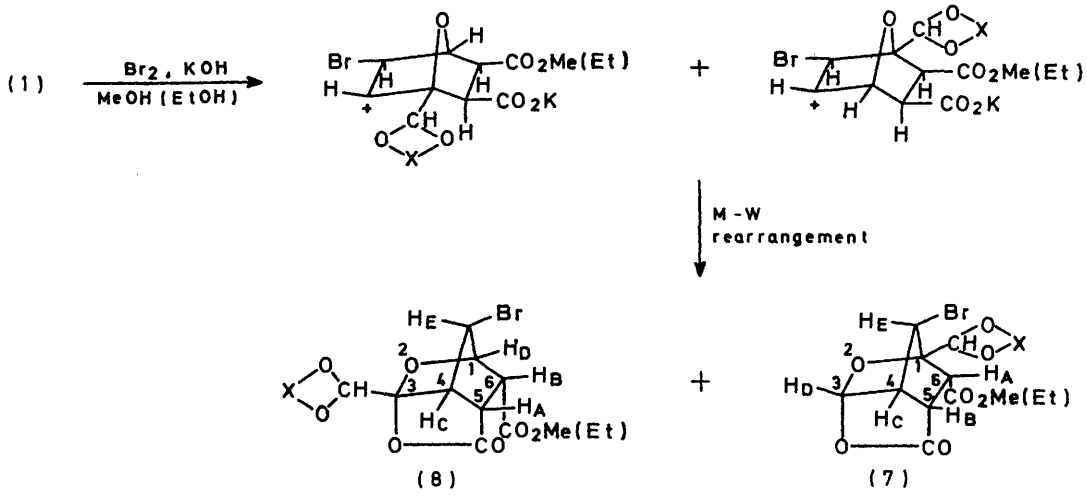
The i.r. spectra of the dibromo-anhydrides (4) showed two peaks at 1790 and 1880 cm^{-1}, corresponding to the

anhydride carbonyl groups. The ^1H n.m.r. parameters, in particular the coupling constants ($J_{5,6}$ 3·1 Hz), showed conclusively that the vicinal protons H-5 and -6 of the dibromo-adducts were in the *trans*-position. Since 1-(1,3-dioxan-2-yl)-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydrides [(1) and (2)] have no symmetry at C-1 and -4, two isomers of the *trans*-dibromo-adducts [(3) and (4)] should be expected to be formed. These pairs of dibromo-adducts may be distinguished by their $J_{4,5}$ values. In the n.m.r. spectra of the dibromo-adducts the H-4 signal appears as a singlet, from which it follows that the ring protons at C-5 and -4 are *endo,exo*-disposed [6] and the compounds have structure (4). The i.r. spectra of the bromo-lactone acids (5) and (6) showed characteristic absorptions for the lactone group at 1795—1820 cm^{-1} and for the acid group at 1715—1725 cm^{-1}. The formation of the bromo-lactone acids from the adducts obtained at 0—20 °C may be explained in terms of the mechanism described by Woodward and Baer.[7] This reaction can proceed only in the presence of some water and if the adduct (2) has the *endo*-configuration.

Esterification of the bromo-lactone acids (5) and (6) with diazomethane yielded a mixture of two bromo-lactone esters, which were separated by fractional crystallization. These products were compared with the bromo-lactone esters obtained from a mixture of the adducts (1) and (2) by brominating their methyl(ethyl) ester potassium salts. This latter reaction gave a mixture of four bromo-lactone esters (5)—(8), of which two [(5) and (6)] were identical with the products derived from direct bromination. Compounds (7) and (8) were identical with the bromo-lactone esters obtained by bromination of the methyl(ethyl) ester potassium salts of the adduct (1) (Scheme 2).

The formation of compounds (7) and (8) can be explained on the basis of a Wagner–Meerwein rearrangement similar to that involved in the lactone formation from *exo*-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride.[7]

The stereochemistry of the bromo-lactone esters (5)—(8) was unambiguously confirmed by their n.m.r. spectra. Data for the products derived from the 2-(2-furyl)-5,5-dimethyl-1,3-dioxan–maleic anhydride adduct are given in Table 3. The coupling constants of H_A and H_B (J 10·2—11·5 Hz) prove their *exo*-positions in all four cases. Compounds (5) and (6) were distinguished from (7) and (8) by the H_C signal, which in (5) and (6) occurs at lower field (by *ca.* 80 Hz), owing to deshielding by the oxygen atom. Moreover, the doublet corresponding to H_D in (7) is at low field (τ 3·8—3·9) owing to the combined effects of the two adjacent oxygen atoms. As might be expected on simple electronegativity grounds the acetal proton in (8) produces a signal at lower field



SCHEME 2

TABLE 3

Chemical shifts (τ) and coupling constants (Hz) for the isomeric bromo-lactones (5f), (6f), (7f), and (8f)

Compound	H_C	H_E	H_A	H_B	H_D	J_{CD}	J_{BD}	J_{BC}	J_{CE}	J_{AB}
(5f) [a]	477 (d)	4·87 (s)	6·29 (d)	6·75 (q)	4·3 (t)	4·5	4·5	0	0	11·5
(6f) [b]	4·9br (s)	5·16	6·87 (d)	6·4 (q)	5·01 (d)	0	4·5	0	0	11·5
(7f) [a]	6·4 (m)	5·52	6·55 (d)	6·95 (q)	3·85 (d)	3·0	0	4·5	1·5	10·55
(8f) [a]	6·2 (m)	5·45	6·52 (d)	6·92 (q)	5·35	0	4·5	0	1·5	10·2

[a] Methyl ester. [b] Ethyl ester.

[6] D. Gagnaire and E. Payo-Subiza, *Bull. Soc. chim. France*, 1963, 2627.

[7] R. B. Woodward and H. Baer, *J. Amer. Chem. Soc.*, 1948, **70**, 1161.

(τ 4·5—4·7) than those in compounds (5)—(7). Further confirmation is provided by the coupling constants of all the bromo-lactone esters (Table 3). Gagnaire and Payo-Subiza,[6] who examined a series of 7-oxabicyclo[2.2.1]-hept-2-ene derivatives, gave the following average values of the coupling constants for vicinal protons in these systems: bridge,*endo*, 0; bridge,*exo*, 4·2—5·0; *exo*,*exo*, 11—11·4; *endo*,*endo*, 7, and *endo*,*exo*, 0—3·2 Hz. The n.m.r. spectra of compounds (5)—(8) are consistent with these average values.

The present findings indicate that the ratio of yields of the isomeric bromo-lactones (5)—(8) depends on two factors: the steric effect of the alkyl-substituted 1,3-dioxan ring, governing the direction of initial attack of bromine on the double bond; and the position of attack by bromine (at C-5 or -6). Compounds (5), (7), and (8) are formed by initial attack of the bromine on the acid salt from the *exo*-side, at C-6 in the case of (5) and (7) and at C-5 in the case of (8). The esters (5) were obtained from the *endo*-adducts (2) as the main product of the reaction with the bromine. The isomers (6) were only obtained from the *endo*-adducts (2a and f). The predominance of the bromo-lactone esters (8) obtained from *exo*-adduct is consistent with the previous observations of greater steric hindrance by alkyl groups at C-4 and -6 of the 1,3-dioxan ring than by those at C-5. Such stereochemical influence by the 1,3-dioxan-2-yl substituent controls the preference for the formation of the isomeric bromo-lactone esters (5), (7), or (8).

EXPERIMENTAL

^{1}H N.m.r. spectra were determined with Varian XL-100 and JEOL-60 H instruments. I.r. spectra were determined with a Unicam SP 200 spectrophotometer. The 2-(2-furyl)-1,3-dioxans were prepared according to the published [5] procedure.

Preparation of the Adducts (1) *and* (2).—*General procedure.* All the adducts were prepared in the same manner. Sublimed maleic anhydride (0·1 mol) was dissolved in diethyl ether, benzene, or toluene (100 ml) and an equivalent quantity of the 2-(2-furyl)-1,3-dioxan derivative was added. The solution was kept at 0 °C or at room temperature for several days, or at 60—80 °C for between 15 min and 9 h. The crystals were filtered off and recrystallized.

1-(1,3-*Dioxan*-2-*yl*)-7-*oxabicyclo*[2.2.1]*hept*-5-*ene*-2,3-*dicarboxylic anhydride*. The *exo*-isomer (1a) was obtained at 75 °C (15 min) as white crystals (92%), m.p. 125—126° (from ethanol). The mixture of *endo*- (2a) (56%) and *exo*-isomers was obtained at 0 °C in diethyl ether (5 days); m.p. 85—86°; yield 82% (Found: C, 57·0; H, 4·9. Calc. for $C_{12}H_{12}O_6$: C, 57·1; H, 4·8%).

1-(4-*Methyl*-1,3-*dioxan*-2-*yl*)-7-*oxabicyclo*[2.2.1]*hept*-5-*ene*-2,3-*dicarboxylic anhydride*. The *exo*-isomer complexed with maleic anhydride was obtained at 70 °C (5 h); yield 89%. Crystallization from propan-2-ol gave the pure exo-*isomer* (1b), m.p. 106—107° (Found: C, 58·5; H, 5·1. $C_{13}H_{14}O_6$ requires C, 58·6; H, 5·2%). The mixture of *endo*- (45%) (2b) and *exo*-isomers was obtained at 0 °C (6 days) as white crystals, which were washed with diethyl ether; m.p. 78—94° (Found: C, 57·8; H, 4·8%).

1-(4,6-*Dimethyl*-1,3-*dioxan*-2-*yl*)-7-*oxabicyclo*[2.2.1]*hept*-5-*ene*-2,3-*dicarboxylic anhydride*. The exo-*isomer* (1c) was obtained at 75 °C in toluene (6 h); yield 88%; m.p. 109—109·5° (from propan-2-ol). The mixture of *endo*-(36%) (2c) and *exo*-isomers was obtained at 0° (8 days) and was washed with cold methanol; m.p. 87—89°; yield 68% [Found: C, 58·4; H, 5·1 (for mixture); C, 60·2; H, 5·9 (for *exo*-isomer). $C_{14}H_{16}O_6$ requires C, 60·0; H, 5·75%].

1-(4,4,6-*Trimethyl*-1,3-*dioxan*-2-*yl*)-7-*oxabicyclo*[2.2.1]*hept*-5-*ene*-2,3-*dicarboxylic anhydride*. The exo-*isomer* (1d) was obtained at 70 °C in benzene (7 h); m.p. 104—106°. The mixture of *endo*- (2d) (26%) and *exo*-isomers was obtained at 0—20° (21 days); m.p. 90—93° [Found: C, 61·0; H, 6·0 (for *exo*-isomer); C, 59·2; H, 5·8 (for mixture). $C_{15}H_{18}O_6$ requires C, 61·2; H, 6·15%].

The methyl half-ester corresponding to (1d) had m.p. 118—120° (Found: C, 58·9; H, 6·9. Calc. for $C_{16}H_{22}O_7$: C, 58·9; H, 6·75%), $\nu_{max.}$ 1715 (C=O acid) and 1745 (C=O ester) cm^{-1}, τ [$(CD_3)_2CO$] 3·68 (2H, q, *J* 6·0 Hz, H-5 and -6), 4·72br (1H, s, *J* 1·5 Hz, H-4), 4·8 (1H, s, acetal H), 7·05 (1H, d, H-3), 7·22 (1H, d, *J* 9·15, H-2), 6·45 (3H, s OCH_3), 4·25 (1H, m, CH·O), 8·45—8·97 (11H, m, CH_3 and CH_2), and 0·5br (1H, s, CO_2H).

1-(4,5,6-*Trimethyl*-1,3-*dioxan*-2-*yl*)-7-*oxabicyclo*[2.2.1]*hept*-5-*ene*-2,3-*dicarboxylic anhydride*. The exo-*isomer* (1e) was obtained at 70 °C (9 h) in benzene; yield 86%; m.p. 102—104°. The mixture of *endo*- (2e) (24%) and *exo*-isomers was obtained at 0° (34 days); yield 68%; m.p. 82—92° [Found: C, 61·1; H, 6·0 (for *exo*-isomer); C, 58·2; H, 5·6 (for mixture). $C_{15}H_{18}O_6$ requires C, 61·2; H, 6·15%].

1-(5,5-*Diethyl*-1,3-*dioxan*-2-*yl*)-7-*oxabicyclo*[2.2.1]*hept*-5-*ene*-2,3-*dicarboxylic anhydride*. The *exo*-isomer (1i) was obtained at 70 °C (90 min); yield 95%; m.p. 109—111°. The mixture (46% *endo*) was obtained in toluene (6 days) at 0 °C; yield 89%; m.p. 87—89° (Found: C, 62·5; H, 6·4. Calc. for $C_{16}H_{20}O_6$: C, 62·3; H, 6·55%).

1-(6-*Isopropyl*-5,5-*dimethyl*-1,3-*dioxan*-2-*yl*)-7-*oxabicyclo*-[2.2.1]*hept*-5-*ene*-2,3-*dicarboxylic anhydride*. The exo-*isomer* (1g) was obtained at 0 °C (24 days; 75% yield) and at 70 °C (7 h; 84%); m.p. 103—104° (Found: C, 63·5; H, 7·1. $C_{17}H_{22}O_6$ requires C, 63·35; H, 6·9%).

1-(5-*Ethyl*-5-*methyl*-1,3-*dioxan*-2-*yl*)-7-*oxabicyclo*[2.2.1]-*hept*-5-*ene*-2,3-*dicarboxylic anhydride*. The *exo*-isomer (1h) was obtained at 75 °C (2 h); yield 95%; m.p. 108—110°. The mixture (50% *endo*) was obtained after 5 days at 0 °C; yield 92%; m.p. 92—93° (Found: C, 61·2; H, 6·2. Calc. for $C_{15}H_{18}O_6$: C, 61·2; H, 6·1%). The adducts (1h) and (2h) are isomeric mixtures (isomers not isolated) with different stereochemistry at C-5 of the 1,3-dioxan ring.

Bromination of Adducts.—To a solution of the adduct (0·1 mol) in chloroform or carbon tetrachloride (150 ml) was added bromine (5·5 ml) in one portion. The mixture was kept at room temperature for 24 h. Much hydrogen bromide was evolved in the case of adducts obtained at 0—20 °C. The precipitate (4a, b, f, h, or i) was separated and was identical with the product of direct bromination of the adducts (1). The dibromo-anhydrides (4c, d, g, and e) are rather unstable and are hydrolysed readily at room temperature, especially when exposed to air. By crystallization from alcohols these products were converted into half-esters or diesters ($\nu_{max.}$ 1715 and 1735 cm^{-1}). Concentration of the mother liquor under vacuum yielded the '*endo*'-bromo-lactone acid ($\nu_{max.}$ 1715 and 1815 cm^{-1}).

Dibromide adducts. 5-exo,6-endo-*Dibromo*-1-(1,3-*dioxan*-2-*yl*)-7-*oxabicyclo*[2.2.1]*hepta*-2,3-*dicarboxylic anhydride* (4a) was obtained from the mixture (1a and b) or from (1a); yield 97%; m.p. 235—236° (Found: C, 35·1; H, 3·1; Br,

38·5. $C_{12}H_{12}Br_2O_6$ requires C, 34·95; H, 2·9; Br, 38·8%); τ [$(CD_3)_2CO$] 4·85 (1H, s, acetal H), 5·0 (1H, s, H-4), 5·28 (1H, d, *J* 3·0 Hz, H-5), 5·6 (1H, d, *J* 3·0 Hz, H-6), 5·75 (1H, d, *J* 7·2 Hz, H-2), 6·0 (1H, d, *J* 7·2 Hz, H-3), 6·1—6·6 (4H, m, OCH_2), 7·2—8·2 (1H, m, CH), and 8·5br (1H, d, CH). The corresponding 2-*ethyl ester* had m.p. 165—167° (Found: C, 36·5; H, 4·0; Br, 34·6. $C_{14}H_{18}Br_2O_7$ requires C, 36·7; H, 3·95; Br, 34·9%).

5-exo,6-endo-*Dibromo*-1-(4-*methyl*-1,3-*dioxan*-2-*yl*)-7-*oxabicyclo*[2.2.1]*heptane*-2,3-*dicarboxylic anhydride* (4b) was obtained from (1b); m.p. 207—209° (decomp.); 96% yield (Found: C, 36·7; H, 3·4; Br, 37·2. $C_{13}H_{14}Br_2O_6$ requires C, 36·65; H, 3·3; Br, 37·5%), $J_{2,3}$ 3·1, $J_{5,6}$ 7·1 Hz.

5-exo,6-endo-*Dibromo*-1-(5-*ethyl*-5-*methyl*-1,3-*dioxan*-2-*yl*)-7-*oxabicyclo*[2.2.1]*heptane*-2,3-*dicarboxylic anhydride* (4h), obtained from (1h), had m.p. 233—234° (decomp.); 98% yield (Found: C, 39·6; H, 3·9; Br, 35·2. $C_{15}H_{18}Br_2O_6$ requires C, 39·6; H, 3·95; Br, 35·21%).

5-exo,6-endo-*Dibromo*-1-(5,5-*diethyl*-1,3-*dioxan*-2-*yl*)-7-*oxabicyclo*[2.2.1]*heptane*-2,3-*dicarboxylic anhydride* (4i), obtained from (1i) or the isomeric mixture, had m.p. 206—208° (Found: C, 39·5; H, 4·3; Br, 33·0. $C_{16}H_{20}Br_2O_6$ requires C, 39·7; H, 4·15; Br, 33·1%). The corresponding *diethyl ester* had m.p. 243—244° (decomp.) (Found: C, 44·1; H, 5·7; Br, 29·3. $C_{20}H_{30}Br_2O_7$ requires C, 44·3; H, 5·55; Br, 29·5%); $\nu_{max.}$ 1735 cm^{-1} (CO ester), $J_{2,3}$ 3·3, $J_{5,6}$ 9·4 Hz.

Diethyl 5-exo,6-endo-*Dibromo*-1-(4,6-*dimethyl*-1,3-*dioxan*-2-*yl*)-7-*oxabicyclo*[2.2.1]*heptane*-2,3-*dicarboxylate*, obtained from (1c) (yield 67%), had m.p. 161—163° (Found: C, 42·0; H, 5·0; Br, 30·9. $C_{18}H_{26}Br_2O_7$ requires C, 42·1; H, 5·05; Br, 31·2%).

The monoethyl ester of 5-*exo*,6-*endo*-dibromo-1-(6-isopropyl-5,5-dimethyl-1,3-dioxan-2-yl)-7-oxabicyclo[2.2.1]-heptane-2,3-dicarboxylic acid, obtained from (1g) (yield 78%), had m.p. 144—145° (Found: C, 43·0; H, 5·1; Br, 30·0. Calc. for $C_{19}H_{28}Br_2O_7$: C, 43·2; H, 5·3; Br, 30·3%), $\nu_{max.}$ 1712 (CO acid) and 1738 cm^{-1} (CO ester), τ [$(CD_3)_2CO$] 0·8 (1H, s, CO_2H), 4·8 (1H, s, acetal H), 4·95 (1H, s, H-4), 5·17 (1H, d, *J* 3·6 Hz, H-5), 5·57 (1H, d, *J* 3·6 Hz, H-6), 5·75 (1H, d, *J* 7·2 Hz, H-2), 5·97 (1H, d, *J* 7·2 Hz, H-3), 5·85 (2H, q, *J* 6·8 Hz, $MeCH_2$), 6·2—6·6 (2H, q, *J* 11·7 Hz, OCH_2), 6·85 (1H, d, *J* 3·6 Hz, O·CH), *ca.* 8·0 (1H, m, CH), 8·75 (3H, t, *J* 6·8 Hz, CH_2Me), 8·85 (3H, s, Me-*ax*), 9·2 (3H, s, Me-*eq*), and 9·0 (6H, d, *J* 6·75 Hz, Me_2C).

Bromo-lactone Acids (*Esters*).—To a stirred mixture of the appropriate adduct (0·1 mol) and water (or an alcohol) (200 ml) in an ice–salt bath, potassium hydroxide (0·15—0·21 mol) in water (50 ml) was added. The solution was cooled to 0—5 °C and bromine was added dropwise with constant stirring until a faint colour persisted. Care was taken to maintain the temperature of the mixture below 5 °C. Acidification with hydrochloric acid produced a crystalline precipitate (7), which was collected, washed several times with water, and crystallized from ethanol. The bromo-lactone acids (esters) (5)—(8) were extracted from the mother liquor with chloroform. The organic layer was washed with aqueous 3% sodium hydrogen carbonate, aqueous 5% sodium thiosulphate, and water, then evaporated. The residue was crystallized from alcohol. By fractional recrystallization from ethanol (or propan-2-ol) the isomeric bromo-lactone esters were separated. Compounds (7) and (8) crystallized as fine needles, whereas (5) formed rhombohedra which melted without decomposition to a clear liquid. In contrast, (7) melts with complete decomposition.

Methyl esters of the bromo-lactone acids. Diazomethane was distilled into an ethereal solution of the bromo-lactone acid. After the reaction had ceased, the ether was boiled off and the solid recrystallized from ethanol.

Spectral data for the isomeric bromo-lactone esters. Specimen ^1H n.m.r. parameters for the four isomeric bromo-lactone esters (5)—(8) are given in Table 3. The i.r. spectra showed $\nu_{max.}$ 1730—1735 (CO ester) and 1800—1820 cm^{-1} (CO lactone).

Methyl 5-exo-*Bromo*-4-(1,3-*dioxan*-2-*yl*)-3-*methoxycarbonyl*-7-*oxabicyclo*[2.2.1]*heptane*-2,6-*carbolactone* (5a) was obtained from (2a) in 45% yield; m.p. 164—165° (from ethanol as a second crop) (Found: C, 43·1; H, 4·2; Br, 21·9. $C_{13}H_{15}BrO_7$ requires C, 43·0; H, 4·15; Br, 22·0%).

5-exo-*Bromo*-3-*carboxy*-1-(1,3-*dioxan*-2-*yl*)-7-*oxabicyclo*-[2.2.1]*heptane*-2,6-*carbolactone* (6a) was obtained from the mixture of (1a) and (2a) in 7·5% yield; m.p. 212—214° (from chloroform–ethanol as fourth crop) (Found: C, 41·7; H, 3·6; Br, 22·6. $C_{12}H_{13}BrO_7$ requires C, 41·25; H, 3·7; Br, 22·9%).

7-endo-*Bromo*-1-(1,3-*dioxan*-2-*yl*)-6-*methoxycarbonyl*-2-*oxabicyclo*[2.2.1]*heptane*-5,3-*carbolactone* (7a) was obtained from (1a) in 86% yield; m.p. 238—239° (decomp.) (from ethanol) (Found: C, 43·2; H, 4·2; Br, 21·9%).

5-exo-*Bromo*-3-*ethoxycarbonyl*-4-(4-*methyl*-1,3-*dioxan*-2-*yl*)-7-*oxabicyclo*[2.2.1]*heptane*-2,6-*carbolactone* (5b) was obtained from the mixture of (1b) and (2b) in 32% yield; m.p. 139—141° (from ethanol as a second fraction) (Found: C, 45·9; H, 4·9; Br, 20·5. $C_{15}H_{19}BrO_7$ requires C, 46·05; H, 4·85; Br, 20·45%).

7-endo-*Bromo*-6-*carboxy*-1-(4-*methyl*-1,3-*dioxan*-2-*yl*)-2-*oxabicyclo*[2.2.1]*heptane*-5,3-*carbolactone* (7b) was obtained from the complex of maleic anhydride with (1b) in 41% yield; m.p. 182—183° (from methanol) (Found: C, 43·0; H, 4·3; Br, 21·8%).

7-endo-*Bromo*-6-*ethoxycarbonyl*-3-(4-*methyl*-1,3-*dioxan*-2-*yl*)-2-*oxabicyclo*[2.2.1]*heptane*-5,3-*carbolactone* (8b) was obtained from the complex of maleic anhydride with (1b) in 12% yield; m.p. 220—221° (from ethanol as a second fraction) (Found: C, 46·1; H, 4·7; Br, 20·5%).

5-exo-*Bromo*-4-(4,6-*dimethyl*-1,3-*dioxan*-2-*yl*)-3-*methoxycarbonyl*-7-*oxabicyclo*[2.2.1]*heptane*-2,6-*carbolactone* (5c) was obtained from the mixture of (1c) and (2c) in 23% yield; m.p. 183—184° (from ethanol as a second fraction) (Found: C, 46·1; H, 5·0; Br, 20·2%).

7-endo-*Bromo*-1-(4,6-*dimethyl*-1,3-*dioxan*-2-*yl*)-6-*ethoxycarbonyl*-2-*oxabicyclo*[2.2.1]*heptane*-5,3-*carbolactone* (7c) was obtained from (1c) in 71% yield; m.p. 229—231° (from ethanol) (Found: C, 47·2; H, 5·2; Br, 19·6. $C_{16}H_{21}BrO_7$ requires C, 47·4; H, 5·2; Br, 19·75%).

5-exo-*Bromo*-3-*ethoxycarbonyl*-4-(4,4,6-*trimethyl*-1,3-*dioxan*-2-*yl*)-7-*oxabicyclo*[2.2.1]*heptane*-2,6-*carbolactone* (5d) was obtained from the mixture of (1d) and (2d) in 18% yield; m.p. 176—177° (from ethanol) (Found: C, 48·5; H, 5·6; Br, 18·8. $C_{17}H_{23}BrO_7$ requires C, 48·7; H, 5·5; Br, 19·05%).

7-endo-*Bromo*-6-*methoxycarbonyl*-3-(4,4,6-*trimethyl*-1,3-*dioxan*-2-*yl*)-2-*oxabicyclo*[2.2.1]*heptane*-5,3-*carbolactone* (8d) was obtained from (1d) in 71% yield; m.p. 208—209° (from methanol) (Found: C, 47·2; H, 5·2; Br, 19·1%).

7-endo-*Bromo*-6-*ethoxycarbonyl*-1-(4,5,6-*trimethyl*-1,3-*dioxan*-2-*yl*)-2-*oxabicyclo*[2.2.1]*heptane*-5,3-*carbolactone* (7e) was obtained from (1e) in 24% yield; m.p. 190—191° (decomp.) (from ethanol) (Found: C, 48·6; H, 5·6; Br, 19·0%).

7-endo-*Bromo*-6-*methoxycarbonyl*-3-(4,5,6-*trimethyl*-1,3-*dioxan*-2-*yl*)-2-*oxabicyclo*[2.2.1]*heptane*-5,3-*carbolactone* (8e) was obtained from (1e) in 15% yield; m.p. 214—215° (from ethanol) (Found: C, 47·2; H, 5·1; Br, 19·6%).

7-endo-*Bromo*-1-(6-*isopropyl*-5,5-*dimethyl*-1,3-*dioxan*-2-*yl*)-6-*methoxycarbonyl*-2-*oxabicyclo*[2.2.1]*heptane*-5,3-*carbolactone* (7g) was obtained from (1g) in 18% yield: m.p. 179—181° (from ethanol as a second crop) (Found: C, 49·9; H, 5·9; Br, 18·2. $C_{18}H_{25}BrO_7$ requires C, 49·9; H, 5·75; Br, 18·45%).

7-endo-*Bromo*-3-(6-*isopropyl*-5,5-*dimethyl*-1,3-*dioxan*-2-*yl*)-6-*methoxycarbonyl*-2-*oxabicyclo*[2.2.1]*heptane*-5,3-*carbolactone* (8g) was obtained from (1g) in 72·5% yield; m.p. 228—229° (from propan-2-ol) (Found: C, 49·9; H, 5·8; Br, 18·3%).

5-exo-*Bromo*-4-(5,5-*diethyl*-1,3-*dioxan*-2-*yl*)-3-*methoxycarbonyl*-7-*oxabicyclo*[2.2.1]*heptane*-2,6-*carbolactone* (5i) was obtained from the mixture of (1i) and (2i) in 43% yield; m.p. 166—168° (from ethanol) (Found: C, 48·6; H, 5·6; Br, 19·0%).

7-endo-*Bromo*-1-(5,5-*diethyl*-1,3-*dioxan*-2-*yl*)-6-*methoxycarbonyl*-2-*oxabicyclo*[2.2.1]*heptane*-5,3-*carbolactone* (7i) was obtained from (1i) in 84% yield; m.p. 207—209° (from ethanol) (Found: C, 48·5; H, 5·4; Br, 19·4%).

5-exo-*Bromo*-4-(5,5-*dimethyl*-1,3-*dioxan*-2-*yl*)-3-*methoxycarbonyl*-7-*oxabicyclo*[2.2.1]*heptane*-2,6-*carbolactone* (5f) was obtained from the mixture of (1f) and (2f) in 41% yield; m.p. 164—165° (from methanol) (Found: C, 46·0; H, 5·0; Br, 20·2%).

5-exo-*Bromo*-1-(5,5-*dimethyl*-1,3-*dioxan*-2-*yl*)-3-*ethoxycarbonyl*-7-*oxabicyclo*[2.2.1]*heptane*-2,6-*carbolactone* (6f) was obtained from the mixture of (1f) and (2f) in 11% yield; m.p. 150—151° (from ethanol as a fourth crop) (Found: 47·3; H, 5·2; Br, 19·5%).

7-endo-*Bromo*-1-(5,5-*dimethyl*-1,3-*dioxan*-2-*yl*)-6-*methoxycarbonyl*-2-*oxabicyclo*[2.2.1]*heptane*-5,3-*carbolactone* (7f) was obtained from (1f) in 86% yield; m.p. 223—224° (from ethanol) (Found: C, 46·1; H, 5·0; Br, 20·0%).

7-endo-*Bromo*-3-(5,5-*dimethyl*-1,3-*dioxan*-2-*yl*)-6-*methoxycarbonyl*-2-*oxabicyclo*[2.2.1]*heptane*-5,3-*carbolactone* (8f) was obtained from (1f) in 13·5% yield; m.p. 170—171° (from ethanol as a second crop) (Found: C, 46·2; H, 5·1; Br, 20·4%). The n.m.r. data of compounds (5f), (6f), (7f), and (8f) are given in Table 3.

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