Chemistry of *gem*-Dihalocyclopropanes. XXIII. Reaction of some *gem*-Dibromocyclopropyl Acetals with Methyllithium

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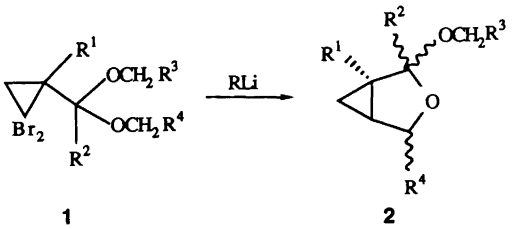
gem-Dibromocyclopropane acetals have been treated with methyllithium to give allenes and monobromides as major products in most cases; bicyclopropylidenes were formed as minor products. Insertion into the acetal C–H bond is observed only for acetals derived from 1,1-dibromo-2-hydroxymethyl-2-methylcyclopropane and vinyl ethers. When 4-(2,2-dibromocyclopropyl)-2-phenyl-1,3-dioxolane is treated with methyllithium at 0 °C, 1-phenylethanol is the predominant product. Reaction mechanisms are discussed.

Insertion into C–H bonds is the most unique reaction of carbenes and is of considerable synthetic potential. We have previously[1] shown that treatment of the *gem*-dibromocyclopropanes (**1**) with methyllithium yields the bicyclic compounds **2**, probably by insertion of an intermediate cyclopropylidene. Strong preference was found for insertion into a C–H bond adjacent to an oxygen atom and 1,5-related to the carbenic carbon. If no hydrogen atom is available at this position, other reactions such as ring opening to allenes become dominant. These observations agree with results obtained by others[2–6] from similar reactions.

In the present work the study of intramolecular C–H insertion of cyclopropylidenes has been extended to acetals derived from *vic* diols and carbonyl compounds or from alcohols and vinyl ethers.

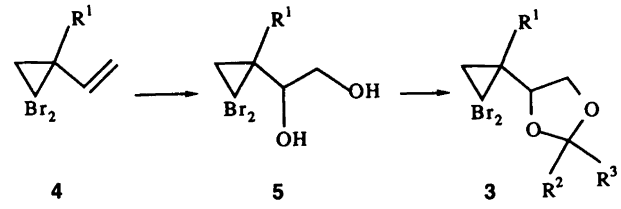


1 2

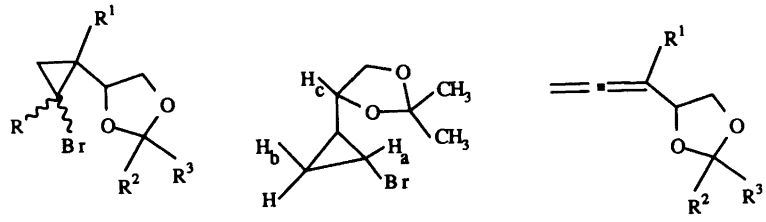
Results

The starting acetals (**3**) were prepared as depicted in Scheme 1. The vinylic *gem*-dibromocyclopropanes (**4**) were readily available using known methods.[7] Catalytic osmium tetroxide oxidations[8] of **4** gave the diols (**5**) as diastereomers in 73–88 % yields. The major diastereomer could be separated by simple fractional crystallisation. Several other oxidation methods[9,10] were tried but either the diols were not formed or they were present only in complex mixtures. Reactions of the major diastereomer of each diol with benzaldehyde, acetaldehyde or acetone afforded the corresponding acetals (**3**) in 64–94 % yields. Each of the acetals **3a–d** consisted of two isomers which differed in the orientation of the substituent on the acetal carbon, but in no case were we able to separate them. However, the structures were ascertained from the NMR spectra of the mixtures, although the configuration of each isomer was not established.

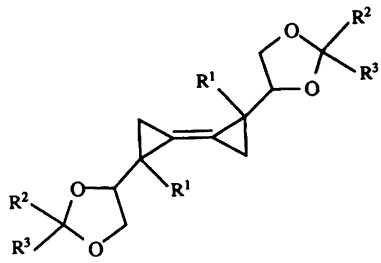
Another structural type of acetal was obtained by protecting the hydroxy group of the cyclopropylcarbinol **6**. The acetals **7**, **8** and **9**, were formed in fair yields, as mixtures of stereoisomers, by treating the alcohol **6** with 2,3-dihydrofuran, 2,3-dihydropyran and ethyl vinyl ether, respectively, as depicted in Scheme 2.



4 **5** **3**



10 **10e** **11**



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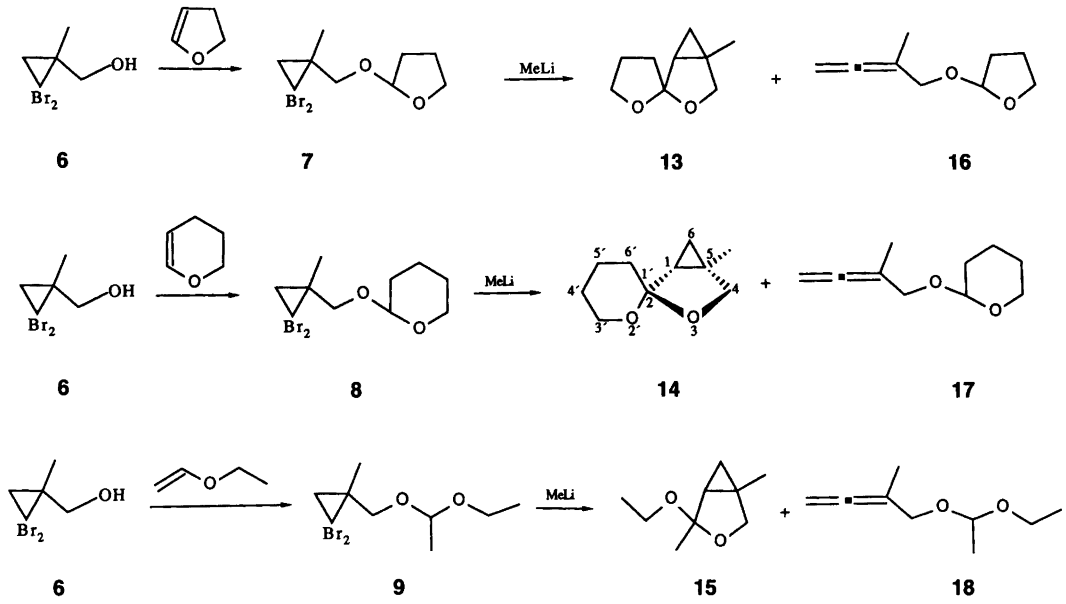
a: R=R¹=R²=H, R³=Ph
b: R=R¹=Me, R²=H, R³=Ph
c: R=R¹=R²=H, R³=Me
d: R=R²=H, R¹=R³=Me
e: R=R¹=H, R²=R³=Me
f: R=H, R¹=R²=R³=Me
g: R=Me, R¹=R²=H, R³=Ph

Scheme 1.

Reactions of the acetal isomer mixtures with methyllithium at either 0 or −78 °C gave in all cases complex products. The results for the acetals **3** are summarised in Table 1. The monobromides **10** and the allenes **11**, were identified as major products in all reactions of the acetals (**3**). The monobromides were in most cases formed as inseparable mixtures of stereoisomers, as revealed from capillary GLC–MS using chemical ionisation. The monobromide **10e** was essentially homogeneous and its configuration was established from NMR data. From successive irradiations, medium to strong n.O.e.'s were observed between the protons a, b and c, which is only compatible with the bromine atom and the acetal moiety being *anti* related. The carbon bearing the bromine gives rise to a signal at δ 68±1 for all the monobromides, and the proton attached to this carbon appears at δ 2.8 for compounds **10a**, **c** and **e**, while the methyl group on the cyclopropane ring causes a downfield shift of this proton to δ 3.15 for compounds **10d** and **f**. These results compare well with data previously published for analogous compound.[1]

According to GLC analysis at least five monobromides were formed from the reaction of **3a** and methyllithium, and a singlet at δ 1.75 in the ^{1}H NMR spectrum suggests that **10g** is a component of the mixture.[1] The allenes **11** were identified by the characteristic absorption in the IR spectrum at 1960 cm^{-1}, and furthermore by their MS and NMR spectra. In the latter the allene group is identified from resonances at δ 70–80 and 85–100 for the trigonal carbons and at



Scheme 2.

δ 205–210 for the central carbon.[11] The data given in Table 1 show that at lower temperatures the monobromides were major product components while at higher temperatures allenes became dominant, which is in accord with the literature.[1,4] The bicyclopropylidene derivative **12c** was isolated and characterised as a mixture of at least four stereoisomers, but analogous compounds were probably present in small amounts in all reactions as indicated by GLC. The NMR spectra compare well with those reported for similar bicyclopropylidene compounds.[5] Interestingly, the reaction of the acetal **3a** with methyllithium affords 1-phenylethanol as major prod-

Table 1. Product distribution of the reaction between the acetals (**3**) and methyllithium.

Entry	*T*/°C	Starting acetal	Product distribution (%)			
			10	**11**	**12**	Not identified
1	0	**3a**	14	86	–	[a]
2	−78	**3a**	76	24	–	[a]
3	0	**3b**	–	95	–	5
4	−78	**3b**	–	95	–	5
5	0	**3c**	38	44	13	–
6	−78	**3c**	86	7	7	–
7	0	**3d**	12	76	–	12
8	−78	**3d**	60	35	–	5
9	0	**3e**	28	42	–	30
10	−78	**3e**	95	5	–	–
11	0	**3f**	11	83	–	6
12	−78	**3f**	75	25	–	–

[a]One equiv. MeLi; more than one equiv. gave substantial amounts of 1-phenylethanol.

uct; using 1.5 equivalents of methyllithium the ratio between 1-phenylethanol, the monobromide **10a** and the allene **11a** was 76:22:2. A similar reaction was not observed for the acetal **3b**.

No insertion products were identified from the reactions of the acetals **3**. However, insertion reactions occurred with the acetals **7**, **8** and **9**, resulting in the spiro compounds **13**, **14** and **15** together with the allenes **16**, **17** and **18**, respectively, as major products. In addition small amounts of monobromides were formed as indicated by GLC–MS, but they were not isolated. The ratio of insertion products to allenes increased in favour of the former when the reaction temperature was reduced from 0 to −78 °C as indicated in Table 2. Pure samples of the spiro compounds and the allenes were obtained by preparative GLC. On a larger scale the spiro compounds were conveniently separated from the isomeric allenes by flash chromatography subsequent to selective acid hydrolysis of the latter to the corresponding alcohols. The allenes were easily identified from their spectral properties, which were similar to those of compounds **11**. The molecular weights of the insertion products **13**, **14** and **15** were obtained from their mass spectra, but the structural assignments rest mainly on evidence from NMR data. The quaternary acetal carbon atom gave rise to a signal in the region δ 105–115.

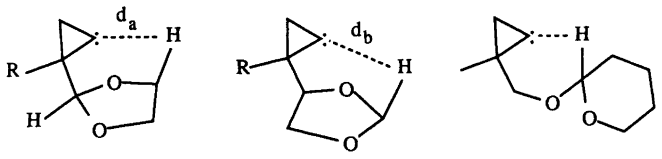
While the acetals **13** and **15** were isolated as approximately 1:1 mixtures of stereoisomers, as revealed by both capillary GLC and ^{13}C NMR spectroscopy, the spiro compound **14** was obtained from **8** as a single isomer and its stereochemistry was established from n.O.e. experiments. The assignment of resonances is based on a detailed analysis of the 400 MHz ^{1}H NMR spectrum. Irradiation of the methylene protons at C-4, which appeared as two doublets at δ 3.67 and 3.72, indicated that the low-field resonance at δ 0.45 corresponds to the *syn* proton at C-6. The double multiplet at δ 1.50 must correspond to one of the protons at C-6′, presumably the equatorial one, and the resonances at δ 3.48 and 3.85 are due to the two C-3′ protons. Moreover, the former resonance must be that of the equatorial hydrogen with one large *geminal* coupling constant and two small *vicinal* ones. The latter resonance should be that of the axial C-3′ proton with two equally large (J_{gem} and J_{aa}) and one small (J_{ae}) coupling constant. Further n.O.e. experiments showed that irradiation of the *syn* proton at C-6 caused an effect on the protons of the 6′-methylene group and not on the protons at C-3′. Irradiation of the 'axial' proton C-4 resulted in an enhancement of the signals for the methyl group and the tertiary proton at C-1, but with no apparent effect on the protons at C-6. The results are consistent with the configuration for **14** depicted in Scheme 2.

Discussion

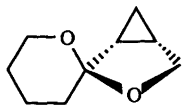
In contrast to our previous results for acetals **1**,[1,4] reactions of compounds **3** with methyllithium gave no 1,5-insertion products. The major products were in all cases the monobromides **10** and allenes **11**. This is surprising especially in view of the high yield (85 %) of the 1,5-insertion product **2** ($R^1=CH_3$, $R^2=H$, $R^3,R^4=CH_2CH_2-$) obtained from the corresponding dioxolane acetal **1** and methyllithium. Several other examples of 1,5-insertions into C–H bonds adjacent to a hetero atom are reported in the literature.[1–6] It has been proposed that lithium of the intermediate bromolithium derivative complexes with the hetero

Table 2. Product distribution from the reaction of the acetals **7**, **8** and **9** with methyllithium.

Entry	*T*/°C	Starting acetal	Product distribution (%)			
			Monobromide	**15**	**16–18**	Not identified
1	−78	**7**	18	42	38	2
2	0	**8**	3	40	50	2
3	−78	**8**	5	75	20	1
4	−78	**9**	11	44	39	6



19 **20** **21**



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atom thereby bringing the carbenyl carbon and the C–H bond close enough for the reaction to take place.[1] It also seems likely that the relative orientation of the *p*-orbital of the carbenyl carbon and the C–H orbital is important. Comparison of models of the carbenes **19** and **20** derived from **1** (R^2=H, R^3,R^4=CH_2CH_2–) and **3a**, respectively, reveals that the distance between the carbenyl carbon and the 1,5-related C–H bond is larger in the latter, i.e. $d_b > d_a$. This, combined with a less favourable orbital orientation, will increase the activation energy for the insertion reaction, and ring opening to allene becomes competitive. Applying the same argument to the reactions of the acetals **7**, **8** and **9**, the complexed intermediate depicted as the free carbene **21** is more flexible, and the C_5–H bond can easily assume a conformation that facilitates the insertion reaction. The difference in reactivity of the acetals **1**, **7**, **8** and **9** vs. **3** indicates strong configurational and conformational demands for the insertion reaction.

The product composition from the acetal **8** contrasts with that obtained by Brinker *et al.*[12] from the reaction of the derivative without the methyl group under similar conditions; they reported a product consisting of the spiro compound **22** (20 %) and monobromides (20 %), but with no trace of allene.

The formation of 1-phenylethanol from **3a** was surprising. The reaction was temperature dependent since at −78 °C and with 1.5 equivalents of methyllithium no alcohol was formed, while under the same conditions at 0 °C a 65 % yield was obtained. Changing the temperature alters the ratio between the allene and the alcohol while the yield of monobromides remains nearly constant. It has been reported[13] that 2-phenyl-1,3-dioxolanes react with organolithium reagents producing 1-phenylalkanols through an initial abstraction of a proton on the dioxolane ring. We believe a similar mechanism may operate in our case, particularly since the stabilising effect of the phenyl group seems essential, although not sufficient, for the reaction to occur, as indicated by the absence of 1-phenylethanol in the product from **3b**. The effect of the methyl group is difficult to rationalise. In our example the proton abstraction may take place either intra- or intermolecularly. In the former case the reaction commences with a methyllithium–bromine exchange, forming the bromolithium intermediate that can either produce the cyclopropylidene, and hence the allene, or abstract a proton intramolecularly. This reaction path is unlikely because the formation of monobromide **10a** does not parallel that of 1-phenylethanol. Additional experiments are certainly required before a mechanism for the alcohol formation can be established.

The monobromides **10** and the bicyclopropylidene compounds **12** are most probably derived from the intermediate bromolithiocyclopropanes. Formation of these products is expected under the reaction conditions, and they have actually been known to be major products.[1] The yields are easily reduced by lowering the concentrations of the reactants.

Experimental

General. The instruments employed have been described elsewhere.[5] Mass spectra are chemical-

ionization spectra, with methane as the ionization gas.

Materials. 1,1-Dibromo-2-vinylcyclopropane (**4a**)[7], 1,1-dibromo-2-methyl-2-vinylcyclopropane (**4b**)[7] and 1,1-dibromo-2-hydroxymethyl-2-methylcyclopropane (**6**)[14] were prepared according to the literature.

1-(2,2-Dibromocyclopropyl)-1,2-ethanediol (**5a**). The title compound was prepared according to a published procedure[8] by adding **4a** (22.6 g, 100 mmol) to a mixture of *N*-methylmorpholine *N*-oxide (16.8 g, 108 mmol), water (50 ml), acetone (20 ml), *t*-butanol (8 ml) and OsO_4 (80 mg, 0.31 mmol). The reaction was stirred for 20 h at room temperature, after which time it was worked up in the usual way to give a yellow oil. GLC analysis showed the oil to contain two components in a 2:3 ratio which were identified as stereoisomers. The crude yield of **5a** was 19.0 g (73 %). The major isomer was isolated by fractional crystallisation from benzene/methanol; m.p. 86–90 °C; IR(KBr): 3250, 3000, 2920, 1430, 1085, 800, 680 cm^{-1}; ^1H NMR [60 MHz, $(CD_3)_2SO$]: δ 1.70 (m, 3H), 3.25 (m, 3H), 4.80 (m, 2H); ^{13}C NMR (15 MHz, CD_3OD): δ 25.66 (C), 27.54 (CH_2), 33.78 (CH), 66.27 (CH_2-OH), 75.68 (CH-OH).

1-(2,2-Dibromo-1-methylcyclopropyl)-1,2-ethanediol (**5b**). This was obtained from **4b** (23.6 g, 100 mmol) by the procedure described for **5a** above. The yield was 21.8 g (88 %) of **5b** as a 2:7 mixture of stereoisomers. The major isomer was isolated by fractional crystallisation from benzene/methanol, m.p. 114–116 °C; IR(KBr): 3300, 3000, 2920, 1420, 1050, 760, 680 cm^{-1}; ^1H NMR [60 MHz, $(CD_3)_2SO$]: δ 1.23 (s, 3H), 1.4–2.0 (m, 2H), 3.3–3.7 (m, 3H), 4.5–5.0 (m, 2H); ^{13}C NMR (15 MHz, CD_3OD): δ 18.96 (CH_3), 32.61 (C), 35.54 (CH_2), 35.93 (C), 64.58 (CH_2-OH), 78.94 (CH_2-OH).

General procedure for the formation of the acetals **3**. The major stereoisomer of each of the diols **5**, an excess of the carbonyl compound (benzaldehyde, acetaldehyde or acetone) and a trace of *p*-toluenesulfonic acid were dissolved in benzene or methylene chloride. The mixture was heated under reflux and the water was separated with a Dean–Stark trap. The reaction was monitored by GLC. The solution was cooled, washed with 10 % Na_2CO_3 and dried ($MgSO_4$). Evaporation of the organic layer followed by column chromatography of the residue on silica gel [eluent: ethyl acetate/petroleum ether (b.p. 40–60 °C); 1:8] gave the acetals **3a–d** which were isolated as mixtures of stereoisomers.

4-(2,2-Dibromocyclopropyl)-2-phenyl-1,3-dioxolane (**3a**). The reaction resulted in a 1:1 mixture of *cis/trans* isomers as a liquid in 83 % yield. IR (film): 3015, 2940, 2870, 1600, 1490, 1450, 1385, 1085, 750, 690 cm^{-1}; ^1H NMR (60 MHz $CDCl_3$): δ 1.7–2.0 (m, 3H), 3.9–4.5 (m, 3H), 5.75 and 5.93 (2s, 1H), 7.39 (bs, 5H); ^{13}C NMR (15 MHz, $CDCl_3$): δ 22.48 (C), 28.13 (CH_2), 32.94, 33.52 (CH), 70.04 (CH_2O), 78.87, 79.59 (CHO), 103.76, 104.34 (acetal CH), 126.56, 128.45, 129.49, 137.02, 137.41 (Ph).

4-(2,2-Dibromo-1-methylcyclopropyl)-2-phenyl-1,3-dioxolane (**3b**). A 3:5 mixture of *cis/trans* isomers was obtained as a liquid in 64 % yield. IR (film): 3020, 2940, 2880, 1600, 1500, 1460, 1380, 1090, 750, 690 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$): δ 1.35, 1.40 (2s, 3H), 1.56 (d, *J* 8 Hz, 1H), 1.75 (d, *J* 8 Hz, 1H), 4.15 (m, 3H), 5.65 (major isomer), 6.05 (minor isomer) (2s, 1H), 7.4 (m, 5H).

4-(2,2-Dibromocyclopropyl)-2-methyl-1,3-dioxolane (**3c**). The crude product was isolated as a liquid in 82 % yield, which consisted of a 1:1 ratio of *cis/trans* isomers. ^1H NMR (60 MHz, $CDCl_3$): δ 1.40 (m, 3H), 1.85 (m, 3H), 4.05 (m, 3H), 5.00 (m, 1H); ^{13}C NMR (15 MHz, $CDCl_3$): δ 19.81, 19.94 (CH_3), 22.54 (C), 27.93, 28.13 (CH_2), 33.00, 33.85 (CH), 69.71, 70.04 (CH_2O), 78.48 (CHO), 101.55, 102.07 (acetal CH).

4-(2.2-Dibromo-1-methylcyclopropyl)-2-methyl-1,3-dioxolane (**3d**). This was obtained in 94 % yield as a liquid which consisted of a 7:3 ratio of *cis/trans* isomers: ^1H NMR (60 MHz, $CDCl_3$): δ 1.53 (s, 3H), 1.54 (d, *J* 5 Hz, 3H), 1.58 (d, *J* 8 Hz, 1H), 1.82 (d, *J* 8 Hz, 1H), 4.0 (m, 3H), 5.00 (q, *J* 5 Hz, 1H, major isomer), 5.33 (q, *J* 5 Hz, 1H, minor isomer); ^{13}C NMR (15 MHz, $CDCl_3$): δ 17.34, 17.64 (CH_3), 19.16, 20.23 (CH_3), 30.66, 31.02, 32.35, 33.16 (C), 34.98 (CH_2), 66.95, 67.60 (CH_2O), 81.89, 82.02 (CHO), 102.00, 102.82 (acetal CH).

4-(2,2-Dibromocyclopropyl)-2,2-dimethyl-1,3-dioxolane (**3e**). This was obtained as a liquid in 75 % yield. ^{1}H NMR (60 MHz, $CDCl_3$): δ: 1,37 (s, 3H), 1,47 (s, 3H), 1.6–2.0 (m, 3H), 3.8–4.5 (m, 3H); ^{13}C NMR (15 MHz, $CDCl_3$): δ 22.61 (CH_2), 25.53 (CH_3), 26.77 (CH_3), 28.07 (C), 33.54 (CH), 69.87 (CH_2O), 78.94 (CHO), 109.54 (acetal C).

4-(2,2-Dibromo-1-methylcyclopropyl)-2,2-dimethyl-1,3-dioxolane (**3f**). This was obtained as a solid in 85 % yield, m.p. 27–28 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.34 (s, 3H), 1.38 (s, 3H), 1.50 (s, 3H), 1.54 (d, *J* 7.8 Hz, 1H), 1.79 (d, *J* 7.8 Hz, 1H), 3.96 (m, 2H), 4.26 (dd, J_1 6.3 Hz, J_2 6.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 17.26 (CH_3), 24.69 (CH_3), 26.18 (CH_3), 30.40, 33.09, 34.94 (CH_2, 2×C), 66.16 (CH_2O), 81.64 (CHO), 109.49 (acetal C).

2-(2,2-Dibromo-1-methylcyclopropylmethoxy)tetrahydrofuran (**7**). A solution of **6** (1.22 g, 5 mmol) in 2,3-dihydrofuran (6 ml) was cooled to −30 °C and conc. HCl (one drop) was added. The mixture was stirred for 2.5 h and then slowly heated to room temperature, whereupon 10 % aqueous Na_2CO_3 (6 ml) was added. The reaction mixture was extracted with ether, and the combined organic phases were washed with water, dried ($MgSO_4$), and evaporated. Column chromatography of the residue on neutral alumina [light petroleum (b.p. 40–60 °C)/ethyl acetate; 98:2] afforded 0.63 g (40 %) of **7** as stereoisomers in a 3:2 ratio; MS: 316, 314, 312 (M^+); ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.45 (m, 5H), 1.95 (m, 4H), 3.4–4.1 (m, 4H), 5.15 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.09, 21.16 (CH_3), 23.35, 23.46 (CH_2), 29.18, 29.67, 35.77, 36.14 (C), 32.32 (CH_2), 32.78, 32.89 (CH_2), 66.97, 67.06 (CH_2O), 72.68, 72.94 (CH_2O), 103.54, 103.76 (OCHO).

2-(2,2-Dibromo-1-methylcyclopropylmethoxy)tetrahydrofuran (**8**). The title compound was prepared by dissolving **6** (12.9 g, 53 mmol) in 3,4-dihydropyran (8.4 g, 100 mmol). The reaction was stirred for 1 h, whereupon K_2CO_3 was added. The solvent was evaporated off and the residue was distilled to give 14.7 g (84 %) of **8** as a 3:2 mixture of stereoisomers; b.p. 83–85 °C/0.03 mmHg; ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.43 (s, 3H), 1.50 (brs, 2H), 1.8–2.0 (m, 4H), 3.3–3.9 (m, 4H), 5.13 (brs, 1H).

1-(2,2-Dibromo-1-methylcyclopropylmethoxy)-ethyl ethyl ether (**9**). Following the procedure described for **7**, the dibromo alcohol **6** (1.27 g, 5 mmol) and ethyl vinyl ether (24 ml) gave 0.85 g (54 %) of **9** after column chromatography [neutral alumina; light petroleum (b.p. 40–60 °C)/ethyl acetate; 98:2]; ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.20 (t, *J* 7 Hz, 3H), 1.35 (d, *J* 5 Hz, 3H), 1.50 (s, 3H), 1.60 (m, 2H), 3.65 (m, 4H), 4.80 (q, *J* 5 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 15.20 (CH_3), 19.49, 19.75 (CH_3), 21.11 (CH_3), 29.43, 29.62 (C), 32.74 (CH_2), 35.73, 35.93 (C), 60.81, 60.94 (CH_2O), 70.69, 71.21 (CH_2O), 99.47, 99.73 (OCHO).

Reactions of the acetals **3** *and* **7–9** *with methyllithium. General method.* To a stirred solution of the acetal **3** (10 mmol) in dry ether (25 ml), kept either at −78 or 0 °C, was added dropwise methyllithium (12 mmol of a 1.5*M* solution in ether). After 1 h at the temperature stated the reaction mixture was slowly warmed to room temperature, at which it was further stirred for 6–18 h. The reaction was monitored by GLC. Water was added and the ethereal layer was separated, washed with brine, dried ($MgSO_4$), and analysed by GLC. The products were isolated by distillation and/or preparative GLC. The results are collected in Tables 1 and 2.

Reaction of **3a** *with methyllithium.* At 0 °C with 1.5 equiv. of methyllithium, three major products were formed in the ratio 65:20:15 which were isolated by preparative GLC. The major isomer was found to be 1-phenylethanol by comparison of its spectroscopic data with that of an authentic sample. The second product (20 %) consisted of at least five, presumably stereoisomeric, monobromides (**10a,g**), and the minor component was identified as the allene **11a** present as a 1:1 ratio of stereoisomers: *4-(2-Bromocyclopropyl)-2-phenyl-1,3-dioxolane* (**10a**): MS: 268, 270 (M^+); *4-(2-bromo-2-methylcyclopropyl)-2-phenyl-1,3-dioxolane* (**10g**): MS: 282, 284 (M^+); *2-phenyl-4-(1,2-propadienyl-1,3-dioxolane* (**11a**): MS: 188 (M^+); ^{1}H NMR (60 MHz, $CDCl_3$): δ 4.15 (m, 2H), 4.85 (m, 3H), 5.25 (m, 1H), 5.80, 5.90 (2s, 1H), 7.50 (m, 5H); ^{13}C NMR (15 MHz, $CDCl_3$): δ 70.10 (CHO), 74.07, 75.23 (CHO), 77.25, 77.51 (C=), 89.72, 89.98 (C=), 103.43, 104.47 (C), 126.50, 126.69, 128.38, 129.33, 129.75, 137.80, 137.60 (Ph), 209.08 (=C=).

Reaction of **3b**. Only the allene was isolated and was completely characterised as a 3:2 mixture of stereoisomers:
4-(2,3-butadien-2-yl)-2-phenyl-1,3-dioxolane (**11b**): MS: 202 (M^+); IR (film): 1960 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$): δ 1.85 (t, *J* 3 Hz, 3H), 4.10 (m, 2H), 4.80 (m, 3H), 5.90 (s, 1H), 7.30 (m, 5H).
Reaction of **3c**. Three products were isolated: *4-(2-bromocyclopropyl)-2-methyl-1,3-dioxolane* (**10c**) (two isomers), ^1H NMR(60 MHz, $CDCl_3$): δ 1.20 (m, 6H), 2.80 (m, 1H), 3.5–4.3 (m, 3H), 5.00 (m, 1H); ^{13}C NMR (15 MHz, $CDCl_3$): δ 12.86, 13.18 (CH_2), 15.98 (CHBr), 19.62, 19.94, 24,68, 25.27 (CH and CH_3), 69.65, 70.17 (CH_2O), 75.62 (CHO), 101.81 (acetal CH); *2-methyl-4-(1,2-propadienyl)-1,3-dioxolane* (**11c**) (1:1 mixture of stereoisomers), ^1H NMR (200 MHz, $CDCl_3$): δ 1.40 (2d, *J* 4.8 Hz, 3 H), 3.6–4.2 (m, 2H), 4.56 (m, 1H), 4.86 (m, 2H), 5.0–5.3 (m, 2H); The bicyclopropylidene **12c** was obtained as a mixture of at least four stereoisomers: MS: 209 ($M^+ - C_2H_3O$), 79 (100%); ^1H NMR (200 MHz, $CDCl_3$): δ 1.1–1.9 (m, 12H), 3.6–4.2 (m, 6H), 5.0–5.2 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 8.9, 9.0, 9.1 (CH_2), 18.1, 18.4, 18.5, 18.7 (CH), 69.4, 69.6, 69.8, 70.0 (CH_2O), 75.4, 78.6, 79.4 (CHO), 101.3, 101.4, 101.5, 101.8 (acetal CH), 113.1, 113.4, 113.5 (C=C).

Reaction of **3d**. Both the monobromide and the allene were formed and each consisted of two stereoisomers present in a 2:1 ratio: *4-(2-bromo-1-methylcyclopropyl)-2-methyl-1,3-dioxolane* **10d**, MS: 220, 222 (M^+); *major isomer,* ^1H NMR (200 MHz, $CDCl_3$): δ 0.68 (dd, J_1 4.5 Hz, J_2 6.1 Hz, 1H), 1.24 (s, 3H), 1.33 (d, *J* 2.4 Hz, 3H), 1.3 (m, 1H), 3.15 (dd, J_1 4.4 Hz, J_2 8.1 Hz, 1H), 3.5–4.0 (complex abs., 3H), 4.95 (m, 1H); ^{13}C NMR (15 MHz, $CDCl_3$): δ 17.80 (CH_3), 18.71 (CH_2), 19.39 (CH_3), 23.22 (C), 25.82 (C), 68.48 (CH_2O), 78.42 (CHO), 101.71 (acetal CH); *minor isomer,* ^1H NMR (200 MHz, $CDCl_3$): δ 0.68 (dd, J_1 4.5 Hz, J_2 6.0 Hz, 1H), 1.21 (s, 3H), 1.30 (d, *J* 2.4 Hz, 3H), 1.3 (m, 1H), 3.16 (dd, J_1 4.5 Hz, J_2 8.0 Hz, 1H), 3.5–4.0 (compl. abs., 3H), 5.01 (q, *J* 2.4 Hz, 1H); ^{13}C NMR (15 MHz, $CDCl_3$): δ 17.57 (CH_3), 18.71 (CH_2), 20.23 (CH_3), 23.03 (C), 25.82 (C), 69.22 (CH_2O), 77.54 (CHO), 102.65 (acetal CH); *4-(2,3-butadien-2-yl)-2-methyl-1,3-dioxolane* **11d**; MS: 140 (M^+); ^1H NMR (200 MHz, $CDCl_3$): δ 1.40 (m, 3H), 1.75 (m, 3H), 3.91 (m, 2H); 4.52 (m, 1H), 4.76 (m, 2H), 5.06 (m, 1H); ^{13}C NMR (15 MHz, $CDCl_3$): δ 13.77, 15.10 (CH_3), 19.68 (CH_3), 68.54 (CH_2O), 75.82 (C=), 76.53, 77.25 (CHO), 97.65 (C=), 101.29, 102.13 (acetal CH), 206.05, 206.61 (=C=).

Reaction of **3e**. The allene was formed in too small an amount for isolation, but its presence in the mixture was apparent from a band at 1955 cm^{-1} in the IR spectrum; *4-(2-bromocyclopropyl)-2,2-dimethyl-1,3-dioxolane* (**10e**): ^1H NMR (200 MHz, $CDCl_3$): δ 1.15 (m, 2H), 1.35 (s, 3H), 1.40 (s, 3H), 1.45 (m, 1H), 2.82 (m, 1H), 3.70 (m, 1H), 3.90 (m, 1H), 4.12 (m, 1H); ^{13}C NMR (15 MHz, $CDCl_3$): δ 12.92 (CH_2), 15.98 (CH), 24.78 (CH), 25.53 (CH_3), 26.54 (CH_3), 68.93 (CH_2O), 75.56 (CHO), 109.18 (acetal C).

Reaction of **3f**. The monobromide and allene were the major products: *4-(2-bromo-1-methylcyclopropyl)-2,2-dimethyl-1,3-dioxolane* (**10f**): MS: 234, 236 (M^+); ^1H NMR (60 MHz, $CDCl_3$): δ 0.70 (m, 1H), 1.23 (s, 3H), 1.32 (s, 3H), 1.36 (s, 3H), 1.3 (m, 1H), 3.15 (q, *J* 4 Hz, 1H), 3.6–4.2 (m, 3H); *4-(2,3-butadien-2-yl)-2,2-dimethyl-1,3-dioxolane* (**11f**): MS: 154 (M^+); ^1H NMR (60 MHz, $CDCl_3$): δ 1.38 (s, 3H), 1.40 (s, 3H), 1.72 (t, *J* 4 Hz, 3H), 3.95 (m, 2H), 4.70 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 14.09 (CH_3), 25.62 (CH_3), 26.40 (CH_3), 67.71 (CH_2O), 75.91 (CH_2=), 76.56 (CHO), 97.37 (C=), 109.38 (acetal C), 206.27 (=C=).

Reaction of **7**. Only the major components were fully characterised. *5-Methyl-2,3-dioxabicyclo[3.1.0]hexane-2-spirocyclopentane* (**13**), MS: 154 (M^+), ^1H NMR (200 MHz, $CDCl_3$): δ 0.50 (m, 2H), 1.28 (s, 3H), 1.32 (t, *J* 4 Hz, 1H), 1.96 (m, 4H), 3.70 (q, *J* 8 Hz, 2H), 3.93 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 14.23 (CH_2), 16.40 (CH_3), 23.13 (CH_2), 24.64 (C), 29.29 (CH), 32.66 (CH_2), 67.53 (CH_2O), 72.20 (CH_2O), 115.09 and 115.60 (OCO); *2-(2-methyl-2,3-butadienyloxy)tetrahydrofuran* (**16**), ^1H NMR (300 MHz, $CDCl_3$): δ 1.70 (t, *J* 3 Hz, 3H), 1.92 (m, 4H), 3.88 (m, 2H), 4.20 (m, 2H), 4.67 (m, 2H), 5.17 (t, *J* 3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.25, 15.80 (CH_3), 23.43 (CH_2), 32.29 (CH_2), 65.83, 66.97, 68.54 (2 CH_2O), 74.46 (CH_2=), 95.93 (=C=), 102.82 (OCHO), 207.00 (=C=).

Reaction of **8**. *5-Methyl-2,3-dioxabicyclo[3.1.0]hexane-2-spirocyclohexane* (**14**), ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.43 (dd, J_1 4.7, J_2 8.0 Hz, H-6 *anti*), 0.45 (dd, J_1 4.7, J_2 4.1 Hz, H-6 *syn*), 1.26 (s, 3H), 1.27 (dd, J_1 4.1, J_2 8.0 Hz, H-1), 1.50 (dm, J 12.9 Hz, H-e'), 1.55–1.70 (m, 5H), 3.48 (dm, J 11.5 Hz, H-e'), 3.67 (d, J 7.8 Hz, 1H, H-4), 3.72 (d, J 7.8 Hz, 1H, H-4), 3.85 (ddd, $J_{gem} = J_{aa}$ 11.5 Hz, J_{ac} 3.0 Hz, 1H-$3'_a$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.23 (CH_2), 16.53 (CH_3), 20.12 (CH_2), 22.00 (C), 25.42 (CH_2), 31.10 (CH_2), 32.25 (CH), 61.65 (CH_2), 72.16 (CH_2), 105.96 (OCO); *2-(2-methyl-2,3-butadienyloxy)tetrahydropyran* (**17**), IR (film): 1960 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.3–1.9 (m, 9H), 3.4–4.2 (m, 4H), 4.5–4.8 (m, 3H).

Reaction of **9**. *4-Ethoxy-1,4-dimethyl-3-oxabicyclo[3.1.0]hexane* (**15**), ^{1}H NMR (60 MHz, $CDCl_3$): δ 0.50 (m, 2H), 1.35 (m, 10H), 3.62 (m, 4H); ^{13}C NMR (15 MHz, $CDCl_3$): δ 13.96 (CH_2), 16.04, 1656 (CH_3), 19.89 (CH_3), 23.60 (C), 32.60 (CH), 56.64 (CH_2O), 72.97 (CH_2O), 108.05, 108.18 (OCO); *1-ethoxyethyl 2-methyl-2,3-butadienyl ether* (**18**); ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.30 (m, 6H), 1.75 (t, J 3 Hz, 3H), 3.55 (m, 2H), 4.05 (t, J 2 Hz, 2H), 4.70 (m, 3H).

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