A Convenient Procedure for the Synthesis of Acetals from α-Halo Ketones

Rolf Carlson,[a,*] Hanna Gautun,[b] Andreas Westerlund[a]

[a] Department of Chemistry, Faculty of Science, University of Tromsø, 9037 Tromsø, Norway
Fax: (+47)-776-44-765, e-mail: rolf.carlson@chem.uit.no
[b] Department of Chemistry, Norwegian Institute of Science and Technology, 7491 Trondheim, Norway

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Abstract: A study for determining the scope and limitations of a procedure for synthesising ethylene acetals from haloketones is presented. The method uses 1,2-bis(trimethylsilyloxy)ethane, BTSE, as reagent and Nafion®-TMS as catalyst. Two procedures have been tested: (A) stoichiometric amounts of the haloketone and BTSE and a catalytic amount of Nafion®-TMS were heated to reflux in chloroform solution, and (B) stoichiometric amounts of the reactants and a catalytic amount of Nafion®-TMS were heated to 90–100 °C in the absence of solvent. The following ketones have been tested: 2-bromo-1-phenyl-1-ethanone, 2-bromo-cyclopentenone, 3-bromo-3-methyl-2-butanone, 3-chloro-3-methyl-2-butanone, 1-bromo-3,3-dimethyl-2-butanone, 1-chloro-3,3-dimethyl-2-butanone, 2-bromocyclohexanone, 2-chloro-1-cyclohexyl-1-ethanone, 1,1-dibromo-3,3-dimethyl-2-butanone, 1,3-dibromo-3-methyl-2-butanone, 1,3-dibromo-2-butanone, 1,3-dibromo-2-propanone, 2-chloro-1-phenyl-1-ethanone, and *endo*-2-bromocamphor. Yields were in the range 57–100% with the exceptions of *endo*-2-bromocamphor which afforded <10% yield and the dibromoketones 1,1-dibromo-3,3-dimethyl-2-butanone and 1,3-dibromo-3-methyl-2-butanone for which the method failed. Factors determining the scope and limitations are briefly discussed. Full experimental details and spectroscopic data of the acetals are given.

Keywords: acetals; 1,2-bis(trimethylsilyoxy)ethane; 1,3-dioxolanes; α-halo ketones; protecting group.

Introduction

Acetal protection of the carbonyl group is a common operation and is mentioned in any textbook on organic chemistry. A thorough compilation of methods for their preparation is given by Green and Wuts.[1] In our studies of functionalized haloketones we needed an efficient procedure for the preparation of ethylene acetals from haloketones. A survey of the vast literature on the synthesis of acetals showed that the number of general methods for their preparation from haloketones are remarkably few in number. It is not possible to say whether this is due to a lack of interest in such compounds or due to difficulties encountered in their preparation. Classical acid-catalyzed treatment with 1,2-ethanediol has been used.[2] One such example of this is given by the *Organic Synthesis* procedure[3a] for the acid-catalyzed reaction of 2-bromo-2-cyclopenten-1-one with 1,2-ethanediol which required 64 h of reflux to afford 80% of the acetal. Attempts to use microwave radiation to increase the rate of the reaction of haloketones with 1,2-ethanediol have also been reported.[4] A paper describing a method which uses a combination of 1,2-ethanediol and chlorotrimethylsilane also reported the formation of the ethylene acetal from α-chloroacetophenone.[5] However, the use of acidic conditions and long reaction time is not recommended for reactions involving haloketones since these compounds may rearrange to yield mixtures of isomeric haloketones in acid medium.[6] A promising method for ethylene acetal synthesis under neutral conditions involves the reaction of carbonyl compounds with 1,2-bis(trimethylsilyloxy)ethane, BTSE, in the presence of trimethylsilyl triflate.[7] Two examples of the use of this method with haloketones have been found in the literature.[8] We have recently used a modification of this method in which trimethylsilyl triflate was replaced by the commercially available Nafion®-TMS, which is a polymeric perfluorosulfonic ester of trimethylsilanol.[9] In the present paper we report that this method can be used also for the preparation of ethylene acetals from haloketones.

Methods and Results

Haloketones

The haloketones **1–14** shown in Figure 1 were studied. Ketones **1–11** were prepared by published procedures, see the Experimental Section for references and physical data. Ketones **12–14** were obtained from commercial sources.

Acetal Formation

We have used two variants of the procedure. *Method A:* For sterically unhindered haloketones, stoichiometric amounts of haloketone and BTSE and a catalytic amount of Nafion®-TMS were heated in refluxing chloroform solution until all starting ketone was consumed. *Method B:* For sterically crowded ketones and dihaloketones, the reactants were heated to 90–100 °C without solvent. The yields obtained are summarized in Table 1 and refer to isolated yields of purified product (>95% pure, GC) after Kugelrohr distillation or flash chromatography on silica gel. The reactions were monitored by gas chromatog-

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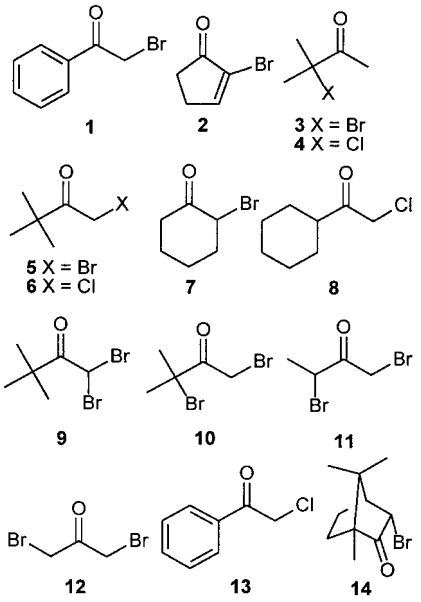


Figure 1. Haloketones investigated.

Table 1. Yields of acetals.

Starting ketone	Method	Reaction time [h]	Yield [%]
1	A	22	94
1	B	4	>99
2	A	10	60
2	B	5	57[a]
3	A	49	73
4	A	20	74
5	B	23	85
5	A	68	100
6	A	68	84
6	B	17	90
7	A	21	97
8	A	67	68
9	A	120	0
9	B	72	0
10	A	404	0
10	B	40	0
11	B	89	90
12	B	9	89
13	B	5	99
14	B	93	<10[b]

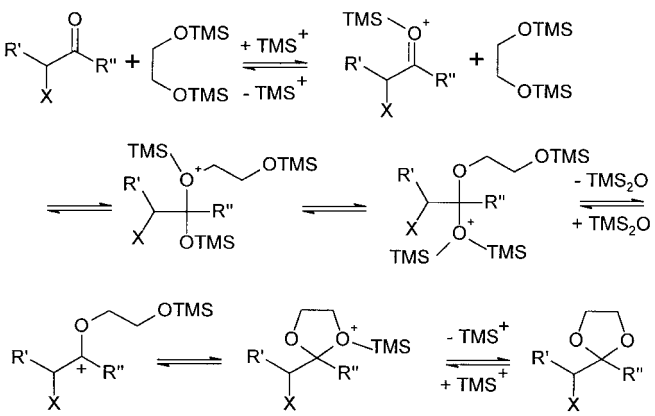
[a] Decomposes.
[b] The product was not isolated, the identity was inferred from its mass spectrum.

raphy and were interrupted when all starting material had disappeared or when there was no further increase in the amount of acetal formed. In the latter case, the pure acetal was obtained by flash chromatography. The identities of the products were inferred from their mass spectrum, ^{1}H and ^{13}C NMR spectra, and IR spectrum.

Discussion

The results show that the present method can be used for the synthesis of ethylene acetals from monohaloketones under almost neutral conditions. We have included sterically crowded monohaloketones in the study to determine whether or not steric effects would inhibit the reaction and thereby limit the scope of the method. The low yield of acetal from bromocamphor shows that severe crowding limits the reaction. 1-Bromo-3,3-dimethyl-2-butanone (**5**) and 1-chloro-3,3-dimethyl-2-butanone (**6**) afford good yields showing that moderate steric hindrance does not reduce the utility of the reaction. For the dibromoketones, 1,3-dibromo-2-butanone (**11**) and 1,3-dibromopropanone (**12**), the reaction affords good yields. However, the reaction time increases considerably going from **12** to **11.** With 1,3-dibromo-3-methyl-2-butanone (**10**) and 1,1-dibromo-3,3-dimethyl-2-butanone (**9**) the method failed. We interpret this largely to be due to the effect of increasing steric hindrance. However, the bromo substituent is isosteric with a methyl group and the observation that 1,1-dibromo-3,3-dimethyl-2-butanone (**9**) affords good yields but 1,3-dibromo-3-methyl-2-butanone (**10**) fails indicate that there is also an electronic component involved. Chan, Brook and Chaly[5] claim that the presence of a halogen substituent alpha to the carbonyl facilitates acetal formation in the procedure when using ethylene glycol and chlorotrimethylsilane. We do not agree with this interpretation and our findings contradict the statement by these authors. Our arguments follow from the tentative mechanism for the conversion of ketones to acetals in the presence of BTSE and chlorotrimethylsilane which is sketched in Scheme 1. This mechanism is very similar to the mechanism proposed in Ref.[5]

If the mechanism in Scheme 1 is correct, an electron-withdrawing α-halo substituent should strongly disfavour the formation of charged intermediates due to severe dipole-dipole repulsion. Hence, one α-halo substituent disfavours acetal formation and two α-halogens may inhibit the reaction.



Scheme 1.

Conclusions

The method described in this paper offers a procedure for preparing ethylene acetals from α-haloketones under neutral conditions. This is an advantage since α-haloketones are prone to rearrange under acidic conditions. The method affords good to excellent yields with moderately congested monohaloketones. With sterically hindered dihaloketones, the methods fails.

Experimental Section

Spectroscopic Methods

^{1}H and ^{13}C NMR spectra were recorded in deuteriochloroform with TMS as internal reference on a Jeol JNM-EX400 spectrometer operating at 400 MHz (^{1}H) and 100 MHz (^{13}C). Mass spectra were taken via gas chromatograph on a VG Quattro or a VG Tribrid instrument. Electron impact ionization (70 eV, 180 °C ion source) was used. In the reported spectra, mass fragments under 5% relative abundance are not included. The mass spectra are reported as follows: *m/z* (relative abundance in %) [assignment]. IR spectra were recorded as neat film between NaCl plates using a Perkin Elmer 1600 Series FT-IR instrument.

Gas Chromatography

A CP-Sil-8 CB open tubular column (0.32 mm i.d.) was used with helium as carrier gas, flow rate 1.5 mL/min. A Varian 3300 gas chromatograph equipped with a FID; injector temperature 250 °C, detector temperature 300 °C. Chromatograms were recorded on a Varian 4400 integrator. For monitoring the reactions, chromatograms were generally taken isothermally at 120 °C, with exception of reactions run with 3-chloro-3-methyl-2-butanone, when a program 40 °C/2 min, 20 °C/min, 120 °C was used.

Chemicals

Solvents (CH_2Cl_2 and $CHCl_3$) were *pro analysi* qualities and supplied from Merck and used as delivered. 1,2-Ethanediol *puriss.* from Fluka was used as delivered. Chlorotrimethysilane from Fluka was distilled. The haloketones were prepared by published procedures, see below. The Nafion®-TMS catalyst was obtained from Aldrich and used as delivered.

Melting points and boiling points are uncorrected.

1,2-Bis(trimethylsilyloxy)ethane, BTSE

A slightly modified literature procedure[10] was used. A 500-mL, three-necked Erlenmeyer flask was charged with 1,2-ethanediol (25 mL, 0.44 mol) and chlorotrimethylsilane (230 mL; a large excess). The flask was fitted with a gas inlet and a reflux condenser coupled to a trap for hydrogen chloride *via* a moisture protective tube with calcium chloride. The resulting two-phase system was magnetically stirred and heated to reflux while a slow stream of dry nitrogen was led through the flask. The reflux was maintained for 50 h during which time the reaction mixture became homogeneous. The reflux condenser was replaced by a 20-cm Vigreux column and unreacted chlorotrimethylsilane was removed by distillation. BTSE was collected at 160 – 168 °C; yield: 74.6 g (82%); ^{1}H NMR: δ = 0.10 (18H, s), 3.61 (4H, s); ^{13}C NMR: δ = 0.4, 63.9; MS: no molecule ion was observed, *m/z* = 193 (10), 192 (24) 191 (57) [M^+-CH3], 150 (5), 149 (39), 147 (100) 134 (5), 132 (43), 131 (28), 117 (9), 115 (10), 105 (8), 104 (11), 103 (48), 101 (12), 89 (8)[Me_3SiO^+], 88 (17), 87 (6), 75 (30), 74 (29), 73 (57) [Me_3Si^+], 67 (10), 66 (34), 61 (9), 60 (5), 59 (30), 58 (14), 52 (11), 47 (11), 45 (29), 44 (14), 43 (25).

Haloketones

2-Bromo-1-phenyl-1-ethanone (**1**) was prepared by bromination of acetophenone in the presence of aluminium trichloride according to Cowper and Davidson.[11] It was recrystallized from ethanol, mp 49 – 50 °C (Lit.[11] 49 – 51 °C).

2-Bromo-2-cyclopentene-1-one (**2**) was prepared from 2-cyclopenten-1-one according to Smith III et al.[3a] It was recrystallized from hexane, mp 35.2 – 35.7 °C (Lit.[3a] 36 – 37 °C, Lit.[3b] 39 – 39.5 °C).

3-Bromo-3-methyl-2-butanone (**3**) and *2-bromocyclohexanone* (**7**) were synthesized from the parent ketone by bromination with *N*-bromosuccinimide analogous to the procedure given by Rappe and Kumar.[12] Bp of **3**: 40 – 42 °C/17 torr (Lit.[12] 40 °C/17 torr); bp of **7**: 84 – 86 °C/15 torr (Lit.[13] 68 °C/2 torr).

3-Chloro-3-methyl-2-butanone (**4**) was obtained by chlorination of the parent ketone with sulfuryl chloride according to Wyman and Kaufman.[14] The pure ketone was obtained by spinning band distillation; bp 113 – 114 °C (Lit.[14] 143 – 145 °C).

1-Bromo-3,3-dimethyl-2-butanone (**5**) and *1,1-dibromo-3,3-dimethyl-2-butanone* (**9**) were prepared by bromination of the parent ketone according to Ramasseul and Rassat.[15] Ketone **5** was purified by fractionation over a Vidmer column, bp 107 °C/80 torr (Lit.[15] 72 – 74 °C/10 torr). Ketone **9** was recrystallized from ethanol, mp 73 – 74 °C (Lit.[15] 74 °C).

1-Chloro-3,3-dimethyl-2-butanone (**6**) and *2-chloro-1-cyclohexyl-1-ethanone* (**8**) were prepared by halogenation of the morpholine enamine of the parent ketone according to Carlson.[16] Bp of **6**: 83 – 85 °C/10 torr (Lit.[17] 110 °C/14 torr), bp of **8**: 98 – 100 °C/10 torr (Lit.[18] 110 °C/14 torr).

1,3-Dibromo-3-methyl-2-butanone (**10**) and *1,3-dibromo-2-butanone* (**11**) were obtained by bromination of the parent ketones in chloroform solution. The pure ketones were obtained by fractionation over a Vidmer column; bp of **10**: 82 – 84 °C/10 torr (Lit.[19] 86 – 88 °C/12 torr), bp of **11**: 103 °C/50 torr (Lit.[20] 64 – 65 °C/2.3 torr).

1,3-Dibromo-2-propanone (**12**) was obtained from Lancaster Ltd., *2-chloro-1-phenyl-1-ethanone* (**13**), was obtained from Fluka and endo-*2-bromocamphor* (**14**) was obtained from Aldrich.

Acetal Synthesis

The reactions were run using 10.0 mmol of the haloketone.

Method A: A 25-mL, round-bottomed flask was mounted with a reflux condenser with a drying tube. The flask was charged with haloketone (10.0 mmol) and BTSE (2.06 g, 10.0 mmol) dissolved in 10 mL of chloroform. The catalyst, Nafion®-TMS (50 mg), was added and the mixture was magnetically stirred and heated to reflux. Samples were taken at time intervals and analyzed by GC. The heating was discontinued when all starting ketone was consumed or when there was no further increase in yield of acetal. The reaction mixture was transferred into a clean flask by using a Pasteur pipette. The solvent was evaporated under reduced pressure and the residue was distilled using a Kugelrohr apparatus.

Method B: A 10-mL, round-bottomed flask was equipped with an air condenser mounted with a drying tube. The flask was charged with haloketone (10.0 mmol), BTSE (2.06 g, 10.0 mmol) and Nafion®-TMS (50 mg). The mixture was magnetically stirred and the flask was placed in an oil bath heated to 90 – 95 °C. Samples (one drop), taken at time intervals, were diluted with dichloromethane and analyzed by GC. The work-up procedure was as above with the exception that the reaction flask was rinsed with three 1-mL portions of dichloromethane which were combined with the crude product prior to evaporation and Kugelrohr distillation.

Physical and Spectral Properties of the Acetals

2-Phenyl-2-bromomethyl-1,3-dioxolane (acetal from **1**): colourless oil, bp 130 °C/12 torr, solidifies on standing, mp 60 – 61 °C, (Lit.[2a] mp 60 – 61 °C). ^{1}H NMR: δ = 3.67 (2H, s), 3.84 – 3.95 (2H, m), 4.13 – 4.24 (2H, m), 7.31 – 7.40 (3H, m), 7.44 – 7.57 (2H, m); ^{13}C NMR: δ = 38.2, 65.9, 107.3, 126.0, 128.4, 128.9, 139.7.

2-Bromo-6,9-dioxa-spiro[4.4]non-2-ene (acetal from **2**): colourless oil, bp 48 °C/ 0.5 mbar (Lit.[3a] 65 – 65 °C/0.7 torr). ^{1}H NMR: δ = 2.14 – 2.18 (2H, m), 2.34 – 2.38 (2H, m), 3.97 – 4.02 (2H, m), 4.15 – 4.20 (2H, m), 6.17 (1H, dd, *J* = 3.2 Hz, *J* = 2.6 Hz); ^{13}C NMR: δ = 28.7, 34.4, 66.0, 117.7, 123.9, 136.7

2-(1-Bromo-1-methyl-ethyl)-2-methyl-1,3-dioxolane (acetal from **3**): colourless oil, bp 58 – 62 °C/14 torr. ^{1}H NMR: δ = 1.50 (3H, s), 1.77 (6H, s), 4.03 (4H, s); ^{13}C NMR: δ = 20.6, 29.6, 66.0, 70.1, 112.0. MS: (no molecule ion was observed), *m/z* = 195 (5), 193 (6) [$M^+ - CH_3$], 129 (14), 114 (17), 113 (7), 99 (11), 88 (7), 87 (100), 69 (11), 57 (16), 45 (6), 43 (60), 42 (6), 41 (22). IR: ν_{max} = 2986, 2884, 1454, 1372, 1260, 1217, 1159, 1137, 1092, 1043, 950, 894, 881, 771, 648, 590 cm^{-1}. HRMS: No molecule ion was observed. High-resolution mass determination was made using the [$M^+ - CH_3$] ion. Observed: 194.984091 and 192.987014; $C_6H_{10}BrO_2$ requires 194.984370 and 192.986416.

2-(1-Chloro-1-methyl-ethyl)-2-methyl-1,3-dioxolane (acetal from **4**): colourless oil, bp 51 – 53 °C/12 torr. ^{1}H NMR: δ = 1.45 (3H, s), 1.59 (6H, s), 4.02 (4H, s); ^{13}C NMR: δ = 20.2, 28.0, 66.0, 73.8, 112.0. MS: No molecule ion was observed, *m/z* = 151 (11), 149 (33) [$M^+ - CH_3$], 129 (19), 113 (15), 88 (20), 87 (100), 85 (8), 79 (8), 77 (21), 73 (9), 69 (14), 67 (15), 57 (28), 53 (8), 45 (11), 44 (6) 43 (64) 42 (10), 41 (34). IR: ν_{max} = 2984, 2886, 1454, 1371, 1253, 1219, 1164, 1095, 1045, 950, 887, 846, 774, 674, 600 cm^{-1}. HRMS: No molecule ion was observed. High-resolution mass determination was made using the [$M^+ - CH_3$] ion. Observed: 151.033243 and 149.036296; $C_6H_{10}ClO_2$ requires 151.033982 and 149.036932.

2-(1,1-Dimethylethyl)-2-bromomethyl-1,3-dioxolane (acetal from **5**): colourless oil, bp 55 – 57 °C/12 torr. ^{1}H NMR: δ = 1.21 (9H, s), 3.72 (2H, s), 3.95 – 4.07 (2H, m), 4.26 – 4.37 (2H, m); ^{13}C NMR: δ = 25.8, 38.1, 40.6, 67.7, 113.0. MS: No molecule ion was observed, *m/z* = 209 (3), 207 (3) [$M^+ - CH_3$], 167 (96), 165 (100), 129 (51), 122 (20), 121 (20) 86 (31) 73 (8), 57 (24), 55 (7), 43 (13), 42 (12), 41 (18). IR: ν_{max} = 2965, 2898, 1478, 1414, 1365, 1246, 1171, 1063, 1042, 982, 955, 823, 674 cm^{-1}. HRMS: No molecule ion was observed. High-resolution mass determination was made using the [$M^+ - CH_3$] ion. Observed: 208.999646 and 207.001291; $C_7H_{12}BrO_2$ requires 209.000020 and 207.002066.

2-(1,1-Dimethylethyl)-2-chloromethyl-1,3-dioxolane (acetal from **6**): colourless oil, bp 73 – 75 °C/12 torr. ^{1}H NMR: δ = 1.20 (9H, s), 3.80 (2H, s), 3.96 – 4.07 (2H, m), 4.23 – 4.33 (2H, m); ^{13}C NMR: δ = 25.7, 40.2, 48.5, 67.7, 113.2. MS: No molecule ion was observed, *m/z* = 165 (3), 163 (9) [$M^+ - CH_3$], 130 (10), 129 (88), 123 (76), 122 (13), 121 (100), 99 (5), 86 (14), 79 (13), 77 (36), 73 (12), 57 (35), 55 (9), 51 (6), 49 (13), 45 (9), 43 (12), 42 (11), 41 (23). IR: ν_{max} = 2964, 2900, 1480, 1422, 1393, 1366, 1172, 1065, 1018, 995, 955, 844, 746 cm^{-1}. HRMS: No molecule ion was observed. High-resolution mass determination was made using the [$M^+ - CH_3$] and [$M^+ - C(CH_3)_3$] ions. Observed: 165.050454 and 163.052189; $C_7H_{12}ClO_2$ requires 165.049632 and 163.052582. Observed: 123.002849 and 121.005229; $C_4H_6ClO_2$ requires 123.002682 and 121.005632.

6-Bromo-2,5-dioxa-spiro[4.5]decane (acetal from **7**): colourless oil, bp 112 – 116 °C/12 torr (Lit.[20] 90.5 – 92.5 °C/5 torr). ^{1}H NMR: δ = 1.30 – 1.42 (1H, m), 1.46 – 1.73 (4H, m), 1.95 – 2.08 (2H, m), 2.15 – 2.25 (1H, m), 3.91 – 4.02 (2H, m), 4.05 – 4.18 (3H, m); ^{13}C NMR: δ = 23.2, 24.1, 34.2, 35.0, 57.2, 65.6, 65,7, 108.0

2-Chloromethyl-2-cyclohexyl-1,3-dioxolane (acetal from **8**): colourless oil, bp 100 – 105 °C/12 torr. ^{1}H NMR: δ = 1.06 – 1.20 (6H, m), 1.75 – 1.89 (5H, m), 3.52 (2H, s), 3.93 – 3.99 (2H, m), 4.01 – 4.07 (2H, m); ^{13}C NMR: δ = 26.2, 26.3, 26.6, 28.5, 66.2, 111.0. MS: No molecule ion was observed, *m/z* = 156 (6), 155 (70) [$M^+ - CH_2Cl$], 123 (42), 121 (100) [$M^+ - C_6H_{11}$], 83 (12), 79 (9), 77 (18), 73 (10), 55 (21), 51 (4), 49 (7) [CH_2Cl^+], 43 (6), 42 (5), 41 (17). HRMS could not be obtained since the substance decomposed during transportation.

2-(1-Bromoethyl)-2-bromomethyl-1,3-dioxolane (acetal from **11**): colourless oil, bp 115 – 118 °C/12 torr (Lit.[21] 118 – 129 °C/12 torr). ^{1}H NMR: δ = 1.69 (3H, d, *J* = 7.3 Hz), 3.57 (1H, d, *J* = 11.7 Hz), 3.79 (1H, d, *J* = 11.7 Hz), 4.45 (1H, q, *J* = 7.3 Hz); ^{13}C NMR: δ = 20.2, 34.5, 50.0, 67.1, 108.6.

2,2-Bis(bromomethyl)-1,3-dioxolane (acetal from **12**): colourless oil, bp 107 – 110 °C/12 torr (Lit.[2a] bp 113 °C/16 torr). ^{1}H NMR: δ = 3.59 (4H, s), 4.12 (4H, s); ^{13}C NMR: δ = 33.7, 66.7, 106.7.

2-Chloromethyl-2-phenyl-1,3-dioxolane (acetal from **13**): colourless oil, bp 128 °C/15 torr, solidifies on standing, mp (from MeOH) 63.6 – 64.1 °C (Lit.[5] 90 °C). ^{1}H NMR: δ = 3.75 (2H, s), 3.92 (2H, m), 4.18 (2H, m), 7.37 (3H, m), 7.51 (2H, m); ^{13}C NMR: δ = 49.5, 65.9, 107.9, 126.1, 128.4, 129.9, 139.8.

Ethylene acetal from endo-*2-bromocamphor:* the compound was identified from its mass spectrum. It was not isolated. MS: no molecule ion was observed, *m/z* = 261 (24) 259, (24) [$M^+ - CH_3$], 197 (21), 195 (100) [$M^+ - Br$], 180 (8), 179 (33), 167 (20), 166 (36), 165 (14), 164 (35), 156 (24), 155 (36), 153 (6), 151 (22), 149 (6), 142 (26), 141 (37), 140 (26), 139 (32), 138 (26), 137 (6), 135 (19), 134 (5), 133 (28), 132 (9), 127 (25), 126 (26), 125 (32), 123 (29), 122 (25), 121 (32), 120 (26), 119 (26), 117 (8), 115 (14), 114 (26), 112 (67), 111 (18), 110 (15), 109 (33), 108 (22), 107 (33), 106 (17), 105 (31), 103 (13), 100 (6), 99 (31), 98 (6), 97 (30), 96 (13), 95 (36), 94 (13), 93 (33), 92 (21), 91 (37), 89 (6), 87 (27), 86 (14), 85 (7), 84 (21), 83 (34), 82 (26), 81 (31), 80 (24), 79 (33), 78 (24), 77 (31), 74 (7), 73 (31), 70 (16), 69 (30), 68 (29), 67 (30), 66 (26), 65 (28), 64 (7), 63 (18), 59 (7), 58 (5), 57 (19), 56 (22), 55 (29), 54 (24), 53 (26), 52 (23), 51 (24), 50 (13), 45 (24), 44 (22), 43 (26), 42 (23), 41 (26).

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