Bicyclo[2.2.2]octane-2-spirocyclohexanes, Part 5 [1]
The Action of Grignard Reagents on Spirodiisophora-3',6-dione
Frederick Kurzer* and Jane E. Hawkes
a Royal Free Hospital School of Medicine (University of London), London NW 3
b King’s College (University of London), London WC 2
Z. Naturforsch. 47b, 1000–1006 (1992); received February 6, 1992
Bicyclo[2.2.2]octane-spirocyclohexane, Spirodiisophoranes, Grignard Reaction
Grignard reagents react with spirodiisophora-3',6-dione exclusively at its 3'-keto-function, yielding 3'-eq-alkyl(or phenyl)-3'-ax-hydroxy­spi­rodiisophor-6-ones. Successive dehydration and monobromination of the methyl homologue yields products, the structural details of which are settled by their 13C NMR spectra.

Introduction
Grignard reagents react readily with alicyclic ketones, normally with formation of tertiary alcohols as expected. Cyclohexanone yields the appropriate alkylcyclohexanols [2, 3], but simultaneous loss of alkylene may result in the formation of cyclohexanol [4]: when this becomes the main product, the process is effectively a reduction [5]. Alternatively, simultaneous dehydration of the tert-alcohol gives rise to substituted cyclohexenes [6] (see Scheme 1). Cyclopentanone reacts analogously, but tends to yield additionally 1-(1-hydroxycyclopentyl)cyclopentan-2-one by an intermolecular condensation [7]. The steric course of the Grignard reaction in the alicyclic environment has been elucidated by extensive studies involving steroid ketones [8]. Recent work has shown that bicyclo[2.2.2]octanones are also convertible into tertiary alcohols by this approach [9].

In the light of this information, both the cyclohexanone and bicyclo[2.2.2]octanone moieties of the spirodisophorone structure are in principle capable of reacting with Grignard reagents. However, as with all reactions [10, 11] except the Birch reduction [1], the 6-keto-group of the 3',6-dione 1 did not participate in the reaction, which resulted in the exclusive formation of 6-keto-3'- tert-alcohols.

Results and Discussion
Treatment of spirodiisophora-3',6-dione 1 with an excess of methyl-, ethyl- or phenylmagnesium halide gave products formulated, on the basis of their spectral and chemical properties, as 3'-eq-alkyl(or phenyl)-3'-ax-hydroxy­spi­rodiisophor-6-ones (2-4). Extended reaction times and the use of increased proportions of the reagents failed to affect the 6-keto-function of the bicyclo[2.2.2]-octane moiety, so that the 3',6-tert-diol was not obtained. The conversion was attended by appropriate IR spectral changes, particularly the narrowing of the keto-band, and the appearance of intense hydroxyl peaks (at ca. 3500 cm⁻¹).

The configuration of the substituents at C-3' is assigned in conformity with established concepts. Unhindered monocyclic ketones react with Grignard reagents to yield the axial and equatorial alcohol side by side, the former predominating, as was shown by a detailed examination [12] of the action of methylmagnesium halides on 4-t-butylcyclohexanone. In the rigid steroid framework, almost exclusive formation of ax-tertiary alcohols is the rule, accounting for 60–100% of the product arising from 6-, 11-, 12- and 15-ketones [7]. These findings are compatible with mechanistic propos-
structures are supported indirectly by the consequent equatorial conformation of the 3'-ethyl- and especially the bulky 3'-phenyl-group (in 3, 4) that would presumably be preferred in accord with fundamental steric principles applicable to the substituted cyclohexane structure [14].

The only reaction known to date which affects the inactive 6-keto-function in spirodisophorones is the Birch reduction [1]. Applied to the methyl homologue 2, it gave near-quantitative yields of the expected 3',6-di-tert-alcohol 5. The endo-configuration of its 6-hydroxy-group is assigned in accord with the preferential formation of endo-conformers in comparable models [1]. The diol was re-convertible into the starting material by chromic acid oxidation (5 → 2), and gave a monoacyl-derivative on treatment with an excess of 3,5-dinitrobenzoyl chloride: in view of the steric constraints that operate in the environment of C-6, the derivative is regarded as the 3'-ester.

Dehydration of the 3'-methyl-homologue 2 by sulphuric acid in glacial acetic acid gave an olefinic product in high yields. Its formulation as 3'-methylspirodisophor-3'-en-6-one rather than the isomeric 2'-ene is based on the 13C NMR spectral evidence (see below). The readiness and course of this dehydration provides additional support for the axial conformation of the 3'-hydroxy-group (in 2 etc.). Since ready 1,2-eliminations in the cyclohexane system are confined almost entirely to groups of diaxial anti-coplanar orientation [7 b, 15], a means of distinguishing axial and equatorial alcohols (including tertiary examples) is available [7 b, 16]. Thus, dehydration of 3α-ax-hydroxy-3β-methyl-5α-cholestan (E) produces the Δ2-olefin (F), while the 3β-equ-hydroxy-epimer (G), having no suitably disposed ring-hydrogen for anti-coplanar elimination, yields by loss of a 3-ax-methyl proton the exocyclic methylene-compound H [17]. A possible 3'-methylene-structure of the present dehydration product corresponding to H is excluded, being incompatible with the observed first order multiplicities of its 13C NMR signals (6s, 2d, 5t, 6q versus required 6s, 1d, 7t, 5q).

Monobromination of the olefin 6 gave good yields of the 2'-halogeno derivative 7. Halogenation in the bicyclo[2.2.2]octane moiety being prohibited [11], reaction occurs in the cyclohexene ring; replacement at the 2'-methylene carbon is in-
dicated by the $^{13}$C NMR spectral changes accompanying the halogenation (see below). Allylic substitution rather than addition to the double bond is favoured with increasing branching of the olefinic structure [18], as in the present example. Comparable allylic brominations occur in disisophorones, being effected equally readily by molecular bromine or N-bromosuccinimide [19]; they are therefore accountable in terms of the familiar free radical chain mechanism [20].

$^{13}$C NMR Spectra

The $^{13}$C NMR spectra of the present compounds (Table I) are assigned by comparison with the relevant spectral information [1, 10, 11, 21], particularly that relating to 3-hydroxyspirodiisophoranes [10]. The most dependable guidance is provided by the spectrum of 3'-ax-hydroxyspirodiisophorane-6-one (J), which has been assigned unequivocally by the INADEQUATE technique [21], and by that of the diol K; their spectral details are included in Table I for direct comparison. The overall data identify the 3'-keto-group of the cyclohexane

Table I. $^{13}$C NMR Spectra of bicyclo[2.2.2]octane-2-spirocyclohexane derivatives and their assignment$^a$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>C-1</th>
<th>C-2</th>
<th>C-3</th>
<th>C-4</th>
<th>C-5</th>
<th>C-6</th>
<th>C-7</th>
<th>C-8</th>
<th>C-9</th>
</tr>
</thead>
<tbody>
<tr>
<td>J</td>
<td>60.2 d</td>
<td>36.9 s</td>
<td>50.4 t</td>
<td>33.5 s</td>
<td>46.9 t</td>
<td>215.8 s</td>
<td>32.0 s</td>
<td>50.3 t</td>
<td>26.8 q</td>
</tr>
<tr>
<td>2</td>
<td>59.8 d</td>
<td>36.7 s</td>
<td>50.3 t</td>
<td>33.9 s</td>
<td>47.6 t</td>
<td>219.4 s</td>
<td>*32.1 s</td>
<td>49.5 t</td>
<td>27.0 q</td>
</tr>
<tr>
<td>3</td>
<td>60.0 d</td>
<td>36.5 s</td>
<td>*50.5 t</td>
<td>33.9 s</td>
<td>*47.6 t</td>
<td>219.6 s</td>
<td>32.1 s</td>
<td>*50.1 t</td>
<td>27.0 q</td>
</tr>
<tr>
<td>4</td>
<td>59.9 d</td>
<td>37.1 s</td>
<td>*50.4 t</td>
<td>33.9 s</td>
<td>47.5 t</td>
<td>219.7 s</td>
<td>*32.2 s</td>
<td>*50.5 t</td>
<td>26.9 q</td>
</tr>
<tr>
<td>K</td>
<td>55.1 d</td>
<td>39.6 s</td>
<td>50.4 t</td>
<td>33.6 s</td>
<td>43.1 t</td>
<td>69.0 d</td>
<td>33.1 s</td>
<td>50.1 t</td>
<td>28.0 q</td>
</tr>
<tr>
<td>5</td>
<td>46.8 d</td>
<td>37.5 s</td>
<td>*50.6 t</td>
<td>34.6 s</td>
<td>43.2 t</td>
<td>68.8 d</td>
<td>*32.4 s</td>
<td>*50.7 t</td>
<td>28.1 q</td>
</tr>
<tr>
<td>6</td>
<td>66.6 d</td>
<td>37.9 s</td>
<td>50.7 t</td>
<td>33.4 s</td>
<td>47.4 t</td>
<td>215.6 s</td>
<td>32.0 s</td>
<td>52.2 t</td>
<td>26.9 q</td>
</tr>
<tr>
<td>7</td>
<td>*65.2 d</td>
<td>37.9 s</td>
<td>47.3 t</td>
<td>35.0 s</td>
<td>46.6 t</td>
<td>215.1 s</td>
<td>*32.0 s</td>
<td>50.2 t</td>
<td>26.9 q</td>
</tr>
</tbody>
</table>

Table I (continued).

<table>
<thead>
<tr>
<th>Compound</th>
<th>C-10</th>
<th>C-11</th>
<th>C-2'</th>
<th>C-3'</th>
<th>C-4'</th>
<th>C-5'</th>
<th>C-6'</th>
<th>C-7'</th>
<th>C-8'</th>
<th>C-9'</th>
</tr>
</thead>
<tbody>
<tr>
<td>J</td>
<td>32.6 q</td>
<td>34.6 q</td>
<td>52.3 t</td>
<td>63.5 d</td>
<td>47.6 t</td>
<td>32.5 s</td>
<td>49.2 t</td>
<td>34.7 q</td>
<td>29.7 q</td>
<td>36.0 q</td>
</tr>
<tr>
<td>2</td>
<td>32.7 q</td>
<td>34.9 q</td>
<td>51.7 t</td>
<td>71.8 s</td>
<td>54.5 t</td>
<td>*31.9 s</td>
<td>49.5 t</td>
<td>33.7 q</td>
<td>29.7 q</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>32.8 q</td>
<td>34.9 q</td>
<td>*52.0 t</td>
<td>73.6 s</td>
<td>*52.9 t</td>
<td>31.9 q</td>
<td>*47.7 t</td>
<td>36.2 q</td>
<td>29.9 q</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>32.8 q</td>
<td>34.9 q</td>
<td>51.9 t</td>
<td>75.9 s</td>
<td>53.8 t</td>
<td>*32.5 s</td>
<td>49.4 t</td>
<td>36.5 q</td>
<td>29.7 q</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>33.0 q</td>
<td>35.2 q</td>
<td>52.1 t</td>
<td>65.3 d</td>
<td>48.7 t</td>
<td>32.2 s</td>
<td>49.2 t</td>
<td>37.8 q</td>
<td>30.0 q</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>33.3 q</td>
<td>35.9 q</td>
<td>52.8 t</td>
<td>72.3 s</td>
<td>*51.1 t</td>
<td>*32.8 s</td>
<td>49.7 t</td>
<td>33.7 q</td>
<td>29.0 q</td>
<td>36.6 q</td>
</tr>
<tr>
<td>6</td>
<td>*32.8 q</td>
<td>34.4 q</td>
<td>43.1 t</td>
<td>130.9 s</td>
<td>128.3 d</td>
<td>30.8 s</td>
<td>48.9 t</td>
<td>32.3 q</td>
<td>27.0 q</td>
<td>24.5 q</td>
</tr>
<tr>
<td>7</td>
<td>32.7 q</td>
<td>34.2 q</td>
<td>*63.8 d</td>
<td>132.0 s</td>
<td>131.9 d</td>
<td>*33.5 s</td>
<td>48.7 t</td>
<td>31.6 q</td>
<td>27.0 q</td>
<td>22.3 q</td>
</tr>
</tbody>
</table>

$^a$ Signals may be interchanged horizontally.

$^b$ The figures refer to the proton noise-decoupled chemical shifts, and the letters s, d, t and q to the first order multiplicities of the individual signals. Shieldings are given in $\delta$ (ppm) downfield from SiMe$_4$. The solvent was deuteriochloroform throughout.

$^c$ The numbering of the carbon atoms of the spiropodiisophorane structure is given in I;

$^d$ the spectra of J and K, previously reported [1, 10], are included for comparison. That of J was originally assigned by the INADEQUATE technique [21];

$^e$ additional signals of the 3'-eq-ethyl-group: 38.2 t (CH$_3$), 7.1 q (CH$_3$);

$^f$ additional aromatic signals: 150.4 s; 126.4 d; 128.0 d (double intensity); 124.4 (double intensity).
moiety as the target of the Grignard reagents, and provide support for the formulation of the olefinic compounds 6 and 7.

The following spectral features merit brief notice: The carbon framework (C-1-C-11) of the unchanging bicyclo[2.2.2]octane moiety, being relatively distant from the structural changes (at C-3'), produces signals of virtually constant chemical shift, which are, moreover, near-identical with those of the reference compound J [10, 21] (or K in the case of the 3',6-diol 5). However, as in the bromo- [11] and hydroxy-derivatives [10], the 6-keto-carbon displays a consistent small response to structural variation in the extended molecule, being here deshielded by 3–7 ppm; such displacements are presumably attributable to non-bonded intramolecular interaction. In the diol 5, the change of the 6-keto- to the 6-tert-hydroxy-group shields the adjacent C-5 carbon atom slightly (ca. –4 ppm) as expected [1]. Its two doublets are differentiated (between C-1 and C-6) for the same reasons and with certain reservations previously given [1].

The more obvious spectral effects of the Grignard reaction occur in the cyclohexane ring. In the saturated examples 2–5, the original low-field 3'-keto-signal (of 1, δ, 209.6 ppm) is replaced by a singlet in the range established for comparable alicyclic tert-alcohols (i.e. 69–77 ppm [13, 22]). The chemical shift of the high-field singlet of C-5' (δ, ca. 32 ppm) is characteristic of a gem-dimethylated carbon in cyclohexane [23, 24], and is barely affected by structural changes within this ring. The spiro-carbon C-2, shared with the bicyclo[2.2.2]octane moiety, also resonates within very narrow limits (at 37–39 ppm), as indeed it does throughout this series of compounds [1, 10, 11, 21].

Of the three triplets remaining after the disposal of the bicyclooctane signals, one appears consistently at 48–49 ppm and another at ca. 52 ppm: these are associated with C-6' and C-2' in comparable 3'-ax-hydroxylated models [1, 10], including the reference compounds J [21] and K [1], and are assigned accordingly. The chemical shift of the remaining triplet, allotted by exclusion to C-4', indicates that the introduction of the 3'-eq-alkyl (or phenyl) substituent deshields the adjacent C-4'–rather than the C-2'-carbon centre; this reasoning and conclusion remain valid even if the somewhat uncertain allotment of the closely spaced C-2' and C-4' signals were reversed.

The preferred location of the olefinic bond in the dehydration product 6 at C-3'–C-4' (rather than C-2'–C-3') is concluded from its effect on the chemical shift of the dimethylated 5'-carbon: its upfield displacement from its very constant value in saturated analogues (δ, 33 to 31 ppm) is attributable to an adjacent C-4'-olefinic centre rather than the more remote C-2'-alternative. Independent support for this formulation is provided by the striking coincidence of the cyclohexene-signals of 6 and those of 1,3,3,5,5-pentamethylcyclohex-1-ene (L [23]), the structural resemblance of which (to 6) is enhanced by its 5,5-gem-dimethyl group simulating the spiro-centre*.

The monobromination of the olefin (6→7) is attended by the exchange of the triplet allotted to C-2' by a doublet in the range characteristic of the 2'-carbon bearing an axial bromo-substituent [11]. Its electron withdrawing effect is also the likely origin of the observed deshielding of the carbon atoms flanking the adjacent double bond.

**Conclusion**

The inertness of the 6-keto-function of the bicyclo[2.2.2]octane moiety of spirodisophorone 1, demonstrated by its uniformly negative response

* In the light of this interpretation, the provisional formulation of “spirodisophor-2‘(or 3‘)-en-6-one” (compound 13 in [10]), which displays the same upfield shift of C-5', may now be settled in favour of the latter alternative. Accordingly, its signals in Table I [10] of C-2' and C-4' need to be interchanged. The doublets of C-2' and C-3' were erroneously entered as singlets in that Table.
to derivatisation [21], reduction by several methods [10], and bromination [11] is seen to persist in the Grignard reaction now described. In contrast, Grignard reagents interact readily with the detached bicyclo[2.2.2]octanone molecule, both saturated [9, 25] and olefinic [26, 27], including examples bearing additional substituents [25, 27]. The inertness of bicyclo[2.2.2]octanone when part of the extended structure (e.g. 1) is therefore ascribed to steric hindrance; this appears to be exerted specifically by the 2-spirocyclohexane attachment, since multiple substitution within the bridged structure (e.g. in 1,3,3,5,6-pentamethylbicyclo[2.2.2]oct-5-en-2-one) is no obstacle to attack by methylmagnesium chloride [27]. It is noteworthy that the 6-keto-group (of 1) does consistently undergo reduction in the Birch reaction [1]; this apparently divergent behaviour may be due to the smaller steric requirement of the one-electron transfer that initiates this process.

Experimental

The equipment used in determining the spectral characteristics of the compounds is specified in Part 1 [21]. This also gives details about reagents, solvents and general procedures, and lists abbreviations that continue to be used. The production of the Grignard reagents in situ, in anhydrous diethyl ether, was initiated by the addition of catalytic quantities of iodine.

3'-ax-Hydroxy-3'-eq-methylspirodiasophor-6-one (2)
[3'-ax-Hydroxy-3'-eq,4,5',5',7,7-hexamethylbicyclo[2.2.2]octane-2-spirocyclohexan-6-one]

To a stirred solution of methylmagnesium iodide [prepared from iodomethane (28.4 g, 200 mmol) and magnesium (1.92 g, 0.08 g.atom) in ether (60 ml)], spirodiasophor-3'-6-dione (1, 5.52 g, 20 mmol) in ether (150 ml) was added dropwise during 10 min, and the stirred mixture boiled under reflux for 5 h. The excess of the Grignard reagent was destroyed by the slow addition of 10% aqueous ammonium chloride. The ethereal phase was washed with water to neutrality, dried over anhydrous sodium sulphate, and the solvent removed under reduced pressure. The residual colourles viscous oil was dissolved in light petroleum (10 ml), which deposited opaque prisms (m.p. 118–120 °C, 4.6 g, 79%). These gave, on further crystallisation from the same solvent (2 ml per g, recovery 90%), microneddles of 2, m.p. 125–126 °C.

IR (KBr): 3490 vs (OH), 2960–2870 vs, 1490 ms, 1465 s (CH₃,CH₂), 1720 vs vbr (CO), 1385 ms, 1365 s (CMe₂), 1345 s, 1215 s (C=O of tert.OH), 1410 ms, 1255 s, 1190 ms, 1145 m, 1105 s, 1075 ms, 960 w, 875 w cm⁻¹.

C₁₉H₃₂O₂ (292.47)
Calcld C 78.0 H 11.0,
Found C 78.3 H 11.2 M 292.

The same product 2 was obtained (80–85%) when the reaction time was extended (30–70 h); reaction at the 6-keto-function did not occur.

3'-ax-Hydroxy-3'-eq-methylspirodiasophor-6-one (2)

A solution of 2 (0.44 g, 1.5 mmol) in pyridine (10 ml), treated with 3,5-dinitrobenzoyl chloride (0.69 g, 3 mmol) was kept at 100 °C for 15 min, then stirred into ice-water (100 ml) containing concentrated hydrochloric acid (10 ml). The precipitated dark-red gum, which failed to solidify, was taken up in ether, and the oil remaining on removal of the solvent from the washed neutral solution dissolved in light petroleum. On storage at 0 °C, the liquid slowly deposited faintly pink prisms (0.59 g, 81%) of the derivative, m.p. 177–178 °C (from acetone).

IR: 3140 m sh, 3060 ms sh (Ar), 2970–2880 vs, 1465 s (CH₃,CH₂), 1720 vs, br (CO of acyl and ring), 1630 s (C=C), 1550 vs br, 1350 vs (N=O), 1395 m, 1370 ms (CMe₂), 1290 vs vbr (C=O of ester), 1165 vs (C=N), 790–780 s d, 735–720 vs (1,3,5-trisub.Ar), 1250 vs, 1210 s, 1075 s, 920 s cm⁻¹.

C₂₆H₃₄N₂O₇ (486.57)
Calcld C 64.2 H 7.0 N 5.8,
Found C 64.1 H 7.2 N 5.7.

3'-ax-Hydroxy-3'-eq-methylspirodiasophor-6-one (2)

To a stirred solution of ethylmagnesium bromide [prepared from ethyl bromide (21.8 g, 15 ml, 200 mmol) and magnesium (1.92 g, 0.08 g.atom) in ether (ca. 150 ml)] was added dropwise during 5 min a solution of 1 (2.76 g, 10 mmol) in ether (100 ml), and the stirred mixture boiled under reflux for 5 h. The solid (2.5 g, 82%) obtained by the usual isolation procedure gave massive prisms of 3, m.p. 86–88 °C (from light petroleum, recovery 65%). After more extended reaction times (up to 40 h), the same product 3 was obtained (45–50%).
IR: 3500 vs (OH), 2970-2860 vs, 1485 ms, 1465 ms, ketospirene 6 (0.55 g, 2 mmol) in glacial acetic acid (10 ml) was treated at room temperature with 60% hydro-acetic acid (10 ml). The resulting precipitate (m.p. 138 °C, 2.0 g, 70%) gave, on crystallisation from ethanol - light petroleum (5 ml each, recovery 70%), lustrous platelets of 4, m.p. 143-144 °C.

During the usual work-up, gave a pale-yellow viscous liquid dissolved in light petroleum (15 ml), deposited to neutrality, and the solvent removed under reduced pressure. The residual pale-yellow viscous oil, dissolved in light petroleum (15 ml), deposited prismatic needles (2.7 g, 92%) of 5, m.p. 193–194 °C (from methanol – light petroleum).

IR: 3420 vs, 3300 vs (OH), 2965–2870 vs, 1475 ms, 1460 s br (CH₃, CH₂), 1715 vs br (CO), 1390 mw, 1365 ms (CMe₂), 1345 s, 1225 s (C – O of tert.OH), 750 s, 700 s (Ar), 1420 ms, 1255 ms, 1060 ms cm⁻¹. 1H NMR (CDCl₃) δ 7.60-7.35 (m, 3H, Ar), 4.93-4.76 (m, 4H, Me), 3.60-3.40 (m, 4H, Me), 2.40-2.20 (m, 4H, Me), 1.70-1.50 (m, 4H, Me).

3'-ax-Hydroxy-3'-eq-phenylspirodiisophorane-3'-en-one (4)

The use of phenylmagnesium bromide [obtained from bromobenzene (39.4 g, 200 mmol) and magnesium (1.92 g, 0.08 g. atom⁻¹)] and 1 (2.76 g, 10 mmol) from bromobenzene (39.4 g, 200 mmol) and magnesium (1.92 g, 0.08 g. atom⁻¹) gave needles (0.33 g, 75%) of 2 (from light petroleum, identified by mixed m.p. 124–125 °C and IR spectrum.

3'-Methylspirodiisophor-3'-en-6-one (6) (dehydration of 2)

A stirred solution of the 3'-ax-hydroxy-3'-eq-methyl-compound 2 (2.92 g, 10 mmol) in glacial acetic acid (10 ml) was treated dropwise with Kiliani’s 10% chromic acid [28] (6 ml, 5 mmol), stirred at room temperature for 1 h, then diluted with water (50 ml) and the excess of the oxidant removed with 10% aqueous sodium sulphite. The resulting crystalline precipitate (m.p. 118–120 °C, 0.37 g, 84%) gave needles (0.33 g, 75%) of 2 (from light petroleum), identified by mixed m.p. 124–125 °C and IR spectrum.

3'-ax-6-endo-Diol 5: Reoxidation to 2

A solution of the diol 5 (0.44 g, 1.5 mmol) in acetone (15 ml) was treated dropwise with Kiliani’s 10% chromic acid [28] (6 ml, 5 mmol), stirred at room temperature for 1 h, then diluted with water (50 ml) and the excess of the oxidant removed with 10% aqueous sodium sulphite. The resulting crystalline precipitate (m.p. 118–120 °C, 0.37 g, 84%) gave needles (0.33 g, 75%) of 2 (from light petroleum), identified by mixed m.p. 124–125 °C and IR spectrum.
bromic acid (10 drops), followed during ca. 10 min by M-bromine in glacial acetic acid (2 ml, 2 mmol) which was decolourised immediately. The liquid was stirred into ice-water (50 ml) and the precipitated solid crystallised from acetone – light petroleum (1:3; recovery ca. 50%), giving small prisms of the monobromo-compound 7, m.p. 176–178 °C.

IR: 2970–2930 vs, 2870 vs, 1480 s sh, 1450 vs, 1440 s (CH$_3$, CH$_2$), 1725–1710 vs (CO), 1395 m, 1375 s (CMe$_2$), 1260 s, 1240 s, 1220 s, 1170–1155 s t, 890 s, 855 s, 690 s cm$^{-1}$.

C$_{19}$H$_2$_3BrO (353.36)
Calcd  C 64.6 H 8.3 Br 22.6
Found  C 64.2 H 8.6 Br 22.7.