

## Chemistry of *gem*-Dihalocyclopropanes. XIII. The Influence of Neighbouring Groups on Reduction of *gem*-Dibromocyclopropanes with Tributyltin Hydride

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When treated with tributyltin hydride (BTH) a number of substituted *gem*-dibromocyclopropyl ketones, alkyl *gem*-dibromocyclopropanecarboxylates and *gem*-dibromocyclopropyl alcohols gave the corresponding monobromocyclopropyl derivatives in 70–95 % yield. The *E* isomer predominated in all cases except one, *viz.* ethyl 2-bromo-1-phenylcyclopropanecarboxylate which was formed in 90 % yield as a 65:35 mixture of the *Z* and the *E* isomers, respectively. Reduction of 7,7-dibromo-4-isopropenyl-1-methylbicyclo[4.1.0]heptan-2-one gave 1-bromo-2,8,8-trimethyltricyclo[3.2.1.0<sup>3,7</sup>]octan-3-one as a minor product.

The importance of electronic and steric effects on the isomeric composition of the monobromocyclopropane derivatives is discussed.

*gem*-Dihalocyclopropanes can be reduced with a variety of reagents.<sup>1–6</sup> Among the simplest and most convenient is tributyltin hydride (BTH) which usually reacts smoothly with *gem*-dibromocyclopropanes to give the corresponding monobromocyclopropanes in good yields.<sup>7</sup> Except for olefinic unsaturation,<sup>7,8</sup> however, the *gem*-dibromocyclopropanes studied have not contained functional groups with which organotin hydrides can react.<sup>9,10</sup> It was therefore of interest to study the reactions between BTH and *gem*-dibromocyclopropanes containing different polar substituents; the results of this investigation are reported here.

### RESULTS

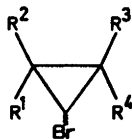
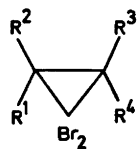
A variety of substituted alkyl *gem*-dibromocyclopropyl ketones, alkyl *gem*-dibromocyclopropanecarboxylates and *gem*-dibromocyclopro-

pyl alcohols were reacted with a 5 % molar excess of BTH at room temperature. Generally the corresponding monobromide was formed in excellent yield as a mixture of the *E* and *Z* isomers. The isomeric ratios were determined by NMR and/or GLC analyses of the reaction mixtures prior to distillation. The results are summarized in Table 1.

The configurations of the bromocyclopropyl ketones and the esters of substituted 2-bromocyclopropanecarboxylic acids were deduced from the <sup>1</sup>H NMR spectra of the isomeric mixtures and those of pure samples of the isomers. The assignments of the structures are based on two assumptions. First of all, it is assumed that in a cyclopropane ring the *cis* coupling constant is larger than the *trans*, an assumption that is in accordance with calculations<sup>11,12</sup> as well as experimental data.<sup>7,13</sup> Secondly, it is assumed that for pairs of isomers the hydrogen atom geminal to the bromine atom gives signals at a lower field for the *E* than for the *Z* isomer due to the anisotropy of the carbonyl group.

Reduction of 1,1-dibromo-2-isobutyryl-2,3,3-trimethylcyclopropane (6) gave the *E* isomer of the corresponding monobromide 22 as the single product. Its NMR spectrum shows a singlet at  $\delta$  3.78 for the hydrogen atom attached to the ring and this is close to the singlet ( $\delta$  3.71) due to the corresponding hydrogen of the *E* isomer of 21 whose *Z* isomer, however, shows a singlet at  $\delta$  2.71.

In order to determine the isomeric compositions of the alcohols 29 and 30 the coupling constants can be employed; for 27, 28 and 31,

Table 1. Reaction of *gem*-dibromocyclopropane derivatives with tributyltin hydride (BTH) at 20°C.

Starting material	Products	<i>E/Z</i> <sup>a</sup>	Yield (%)
R <sup>1</sup> = R <sup>2</sup> = H, R <sup>3</sup> = Me, R <sup>4</sup> = Ac(1)	16	65/35	88
R <sup>1</sup> = H, R <sup>2</sup> = R <sup>3</sup> = Me, R <sup>4</sup> = Ac(2)	17	90/10	70
R <sup>1</sup> = H, R <sup>2</sup> , R <sup>3</sup> = (CH <sub>3</sub> ) <sub>2</sub> , R <sup>4</sup> = Ac(3)	18	84/16	90
R <sup>1</sup> = H, R <sup>2</sup> , R <sup>3</sup> = C <sub>7</sub> H <sub>15</sub> O, R <sup>4</sup> = Me(4) <sup>b</sup>	19	75/25	86
	20 <sup>c</sup>		6
R <sup>1</sup> = R <sup>2</sup> = R <sup>3</sup> = Me, R <sup>4</sup> = Ac(5)	21	93/7	91
R <sup>1</sup> = R <sup>2</sup> = R <sup>3</sup> = Me, R <sup>4</sup> = C <sub>4</sub> H <sub>9</sub> O <sup>d</sup> (6)	22	100/0	90
R <sup>1</sup> = R <sup>2</sup> = H, R <sup>3</sup> = Me, R <sup>4</sup> = COOMe(7) <sup>e</sup>	23	60/40	88
R <sup>1</sup> = R <sup>2</sup> = H, R <sup>3</sup> = Me, R <sup>4</sup> = COOEt(8) <sup>e</sup>	24	70/30	83
R <sup>1</sup> = R <sup>2</sup> = H, R <sup>3</sup> = Me, R <sup>4</sup> = COOBu(9)	25	73/27	87
R <sup>1</sup> = H, R <sup>2</sup> = R <sup>3</sup> = Me, R <sup>4</sup> = COOEt(10)	26	90/10	86
R <sup>1</sup> = R <sup>2</sup> = H, R <sup>3</sup> = Me, R <sup>4</sup> = CH <sub>2</sub> OH(11)	27	65/35	80
R <sup>1</sup> = R <sup>2</sup> = H, R <sup>3</sup> = Me, R <sup>4</sup> = CH(OH)CH <sub>3</sub> (12)	28	62/38	88
R <sup>1</sup> = H, R <sup>2</sup> = R <sup>3</sup> = Me, R <sup>4</sup> = CH(OH)CH <sub>3</sub> (13)	29	90/10	78
R <sup>1</sup> = H, R <sup>2</sup> , R <sup>3</sup> = (CH <sub>3</sub> ) <sub>2</sub> , R <sup>4</sup> = CH(OH)CH <sub>3</sub> (14)	30	65/35	70
R <sup>1</sup> = R <sup>2</sup> = R <sup>3</sup> = Me, R <sup>4</sup> = CH <sub>2</sub> OH(15)	31	63/37	75

<sup>a</sup> In an *E* isomer the bromine atom and the substituent containing either a carbonyl group or a hydroxyl group are *trans* to each other. <sup>b</sup> (-)-Carvone. <sup>c</sup> 1-Bromo-2,8,8-trimethyltricyclo[3.2.1.0<sup>2,7</sup>]octan-3-one. <sup>d</sup> C<sub>4</sub>H<sub>9</sub>O = isobutyryl. <sup>e</sup> From Ref. 41.

however, there exists no simple criterion that can be used to establish the *E/Z* ratio. One may expect that for the alcohols examined vicinal protons or the protons of a vicinal substituent *Z* to a 1-hydroxyalkyl group absorb at a lower field than the same *E* to such a group; however, the hydrogen atom geminal to the bromine atom in 1-(2-bromo-*cis*-1,3-dimethylcyclopropyl)ethanol (29) exhibits a doublet at  $\delta$  1.77 for the *E* isomer ( $J$  6.5 Hz) and a doublet at  $\delta$  2.50 for the *Z* isomer ( $J$  3.5 Hz), which demonstrates that this assumption is invalid. The isomeric compositions of the alcohols 27, 28 and 31 were therefore determined indirectly; those of 27 and 31 by oxidizing the compounds to the corresponding acids and that of 28 by transforming the alcohol to the corresponding ketone and subsequently establishing the isomeric composition of the products by NMR spectroscopy.

From the reaction of dibromocyclopropane derivative 4 with BTH a monobromo derivative with nearly the same boiling point as the

main product 19 was obtained amounting to 8 % of the total product yield. The absence of IR absorptions above 3000 cm<sup>-1</sup> and between 1600 and 1700 cm<sup>-1</sup> strongly indicates that an intramolecular reaction has taken place; this is supported by the <sup>1</sup>H NMR spectrum which shows no resonance in the olefinic region. Three singlets, each representing 3 protons, at  $\delta$  1.00, 1.22 and 1.30 which must be due to three different methyl groups, are an additional indication that such a process has taken place. The rest of the spectrum consists of the two complex multiplets, one in the  $\delta$  1.38–2.04 region (4 H) and the other between  $\delta$  2.14 and 2.55 (2 H). The most reasonable structure consistent with these data is 1-bromo-2,8,8-trimethyltricyclo[3.2.1.0<sup>2,7</sup>]octan-3-one (20).

In addition to the results summarized in Table 1 treatment of ethyl 2,2-dibromo-1-phenylcyclopropanecarboxylate (32) with BTH gave a 90 % yield of the corresponding monobromo derivative 33 as a mixture of isomers (ratio 65:35) which were separated by prepar-

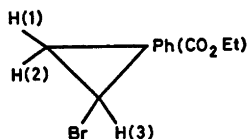


Fig. 1. Numbering of the hydrogen atoms attached to the cyclopropane ring in ethyl 2-bromo-1-phenylcyclopropanecarboxylate (33).

ative GLC. The IR spectra were almost identical, but the NMR spectra showed significant differences as far as the three protons attached to the ring are concerned. For each isomer these protons (Fig. 1) give rise to an AMX spectrum. Their spectra indicate that H(3) is situated *Z* to H(1) in the predominant isomer and *E* to the same hydrogen atom in that formed in lower yield, provided that  $J_{cis} > J_{trans}$ . Accordingly, if H(1) is *cis* to the phenyl group 33 is formed predominantly in the *Z* configuration. Pavia and co-workers<sup>14</sup> have analyzed the NMR spectra of several similar cyclopropane derivatives and they found that the protons *cis* to the phenyl group have a lower chemical shift ( $\delta$  0.95–1.20) than those *trans* to it ( $\delta$  1.47–1.58). For both isomers of 33 the difference in the chemical shifts of H(1) and H(2) due to van der Waals interactions between the bromine atom and each of these protons is small compared with the effect of the benzene ring and the carbonyl group on the same protons; it is therefore reasonable to assume that also for ethyl 2-bromo-1-phenylcyclopropanecarboxylate H(1) is *cis* to the phenyl group. Consequently, ester 33 is formed as a 65:35 mixture of the *Z* and *E* isomers, respectively.

Table 2. Bromocyclopropanes from *gem*-dibromocyclopropane derivatives with tributyltin hydride (BTH). Formula, see Table 1.

R	Notation	<i>syn/anti</i> <sup>a</sup>	Yield (%)	Ref.
R <sup>1</sup> =Ph, R <sup>2</sup> =R <sup>3</sup> =R <sup>4</sup> =H (34)	41	65/35	70	
R <sup>1</sup> =Me, R <sup>2</sup> =vinyl, R <sup>3</sup> =R <sup>4</sup> =H (35)	42	58/42	65	
R <sup>1</sup> =Me, R <sup>2</sup> =isopropenyl, R <sup>3</sup> =R <sup>4</sup> =H (36)	43	43/57	87	
R <sup>2</sup> , R <sup>3</sup> =(CH <sub>2</sub> ) <sub>4</sub> , R <sup>1</sup> =R <sup>4</sup> =H (37)	44	71/29	82	7
R <sup>2</sup> , R <sup>3</sup> =(CH <sub>2</sub> ) <sub>6</sub> , R <sup>1</sup> =R <sup>4</sup> =H (38)	45	87/13	78	
R <sup>1</sup> =R <sup>2</sup> =R <sup>3</sup> =Me, R <sup>4</sup> =H (39)	46	80/20	79	7
R <sup>1</sup> =R <sup>2</sup> =R <sup>3</sup> =Me, R <sup>4</sup> =Et (40)	47	<sup>b</sup>	79	

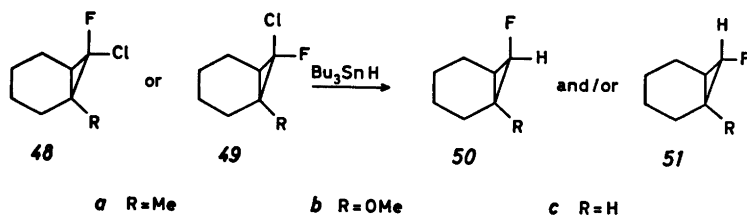
<sup>a</sup> A *syn* isomer has the bromine atom and the largest substituent(s) *cis* to one another. <sup>b</sup> A mixture of isomers in a ratio of 4:1. Which isomer predominated is uncertain.

For comparison several alkylated *gem*-dibromocyclopropanes were reduced with BTH; these results are summarized in Table 2 together with some earlier results.<sup>7</sup> NMR spectroscopy does not provide conclusive evidence for the isomer composition of 1-bromo-2-isopropenyl-2-methylcyclopropane (43). Therefore the *anti* isomer was prepared stereospecifically, and comparison of the spectral properties of this compound with those of both isomers of 43 reveals that *anti*-1-bromo-2-isopropenyl-2-methylcyclopropane is the predominant one.

## DISCUSSION

Besides reducing organic halides to the corresponding hydrocarbons,<sup>7,15</sup> organotin hydrides can react with different organic functions such as olefinic and acetylenic unsaturation<sup>9</sup> and the carbonyl group of aldehydes and ketones.<sup>10</sup> From the reactions of BTH with *gem*-dibromocyclopropyl ketones and esters, however, no alcohols or aldehydes were detected and consequently the attack on the bromine atom is much faster than the attack on the carbonyl group. A corresponding regioselectivity was observed in the reduction of *gem*-dibromocyclopropyl derivatives containing a C=C bond (Tables 1 and 2). Similarly it is evident from the yields that BTH also reacts much faster with a C–Br bond than it does with a hydroxyl group (Table 1).

It is generally accepted that tin hydride reductions of alkyl-substituted *gem*-dibromocyclopropanes involve a radical intermediate<sup>15</sup> whose structure is pyramidal<sup>16</sup> and which inverts configuration rapidly through a planar



Scheme 1.

radical.<sup>7,17,18</sup> The cyclopropyl radical is generated by attack of the bulky tributyltin radical at the less hindered C–Br bond.<sup>7</sup> Steric factors then determine the isomeric composition of the monobromocyclopropane derivatives formed in the reaction between the  $\alpha$ -bromocyclopropyl radical and BTH. Thus reduction of 7,7-dibromobicyclo[4.1.0]heptane gave 7-bromobicyclo[4.1.0]heptane consisting mainly of the *syn* isomer (Table 2).<sup>7</sup> Similar results have been published later.<sup>9,19–22</sup>

The configurational stability of a cyclopropyl radical is influenced not only by the  $\alpha$  substituents but also by those in a  $\beta$  position. Thus Ando *et al.*<sup>23</sup> found that the stereospecificity in

the tributyltin hydride reduction of *gem*-dihalocyclopropanes 48 and 49 (Scheme 1) decreased in the order  $a > c > b$ , a sequence which is in agreement with theoretical calculations.<sup>24</sup> These results suggest that the methyl and the methoxy substituents have the effect of stabilizing and destabilizing, respectively, the radical intermediate, a result that is opposite to what is expected from the inductive effect of the substituents alone. It is therefore probable that the methoxy group partly destabilizes the radical by resonance due to contribution from 52 (Fig. 2a).<sup>17</sup> On the other hand, an acyl or an alkoxy carbonyl group in the  $\beta$  position should stabilize a cyclopropyl radical inductively as well as by resonance due to contribution from resonance structure 53 (Fig. 2b) and thus lead to a decrease in the rate of equilibration. A hydroxyl group  $\gamma$  to the radical centre, however, will have only a small influence by induction and none by resonance. Consequently, reduction of the alcohols, esters, and ketones studied here can take place with kinetic or thermodynamic control dependent on the rate of equilibration and accordingly steric as well as electronic factors can affect the course of the reaction.

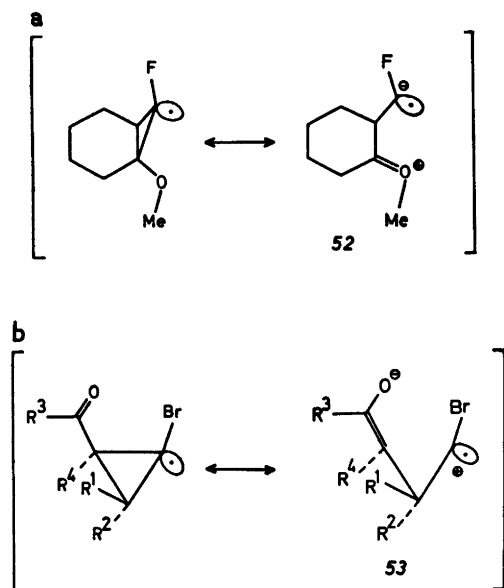
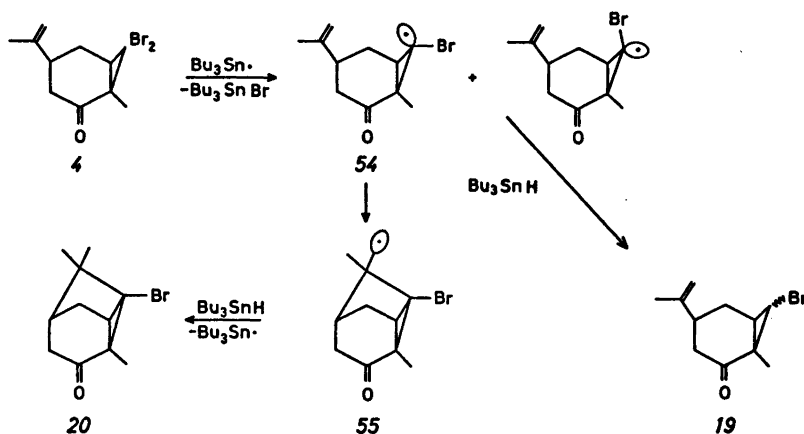


Fig. 2. *a*. Resonance structures of the 7-fluoro-1-methoxybicyclo[4.1.0]hept-7-yl radical. *b*. Resonance structures of a substituted 1-bromocyclopropyl radical containing a carbonyl group  $\alpha$  to the ring.

Evidence for a radical mechanism for the tin hydride reductions of *gem*-dibromocyclopropyl ketones was obtained when the bicyclic heptanone 4 was reduced and gave the tricyclic compound 20 as a minor product. In accordance with the work of Julia<sup>8</sup> and others<sup>25,26</sup> the mechanism for the formation of this compound involves the cyclopropyl radical 54 which attacks the double bond at the more substituted carbon to give 55 and subsequently 20 through a hydrogen transfer reaction (Scheme 2). It is interesting that the attack on the double bond is consistent with Baldwin's rules for ring closure,<sup>27</sup> *i.e.* a 5-*Exo-Trig* rather than a 6-*Endo-Trig* closure takes place.



Scheme 2.

Consistent with a radical mechanism the reduction of *gem*-dibromocyclopropane derivatives 1–15 gave isomeric mixtures of the corresponding monobromides with variable amounts of the *E* and *Z* isomers. However, the results in Tables 1 and 2 indicate, that in addition to steric factors which seem to outweigh all other factors in organotin reductions of alkyl-substituted *gem*-dibromocyclopropanes,<sup>7</sup> electronic interactions may be of importance when substrates 1–15 are reduced with BTH. Thus, an increase in the amount of the *E* isomer was observed when the isopropenyl group in compound 36 and a methyl group in cyclopropane 39 were replaced by an acetyl group (1 and 2, respectively), an ester group (7–9 and 10, respectively) or an  $\alpha$ -hydroxy group (11–12 and 13, respectively).

Concerning the *gem*-dibromocyclopropyl ketones the importance of electronic interactions is supported by several experiments in addition to those already mentioned. When 3 was reduced with BTH the corresponding monobromide was enriched in *syn* isomer (84:16) as compared to 44 (71:29). Further, whereas the monobromides 44, 45 and 46 mainly consisted of the *syn* isomers (Table 2), 7-bromo-4-isopropenyl-1-methylbicyclo[4.1.0]heptan-2-one (19) was composed of the *syn* and *anti* isomers in a ratio of 1:3. Finally, ketones 5 and 6 were reduced almost stereospecifically to the corresponding *E*-monobromocyclopropane derivatives 21 and 22 (Table 1). All these results are opposite to those expected if steric factors were predominant.

With regard to the alcohols the situation is more complicated. The *E/Z* ratios of compounds 27, 28 and 29 were similar to those of the corresponding ketones 16 and 17 and this may indicate that electronic factors determine the isomeric composition. On the other hand, the *E/Z* ratios of the alcohols 30 and 31 were considerably different from those of the corresponding ketones 18 and 21 and this indicates that steric factors predominate. Steric factors therefore seem to be more important when *gem*-dibromocyclopropanes with a hydroxy group  $\alpha$  to the ring are reduced with BTH.

The variation in the *E/Z* ratios of the esters 23–26 is parallel to those of the corresponding alcohols (27–29) and ketones (16 and 17), but our results do not allow us to conclude whether steric or electronic factors mainly determine the isomeric composition.

When the methyl group in  $\delta$  was replaced by a phenyl group the isomeric composition of the monobromide formed changed considerably. Whereas ethyl 2-bromo-1-methylcyclopropanecarboxylate (24) consisted mainly (70%) of the *E* isomer ethyl 2-bromo-1-phenylcyclopropanecarboxylate (33) was composed of 65% of the *Z* and 35% of the *E* isomer. If electronic interactions due to the ester group are predominant when  $\delta$  is reduced with BTH they seem to be unimportant in the reaction between ethyl 2,2-dibromo-1-phenylcyclopropanecarboxylate (32) and BTH. On the other hand, the observed inversion in isomeric composition cannot result from the phenyl group

alone; if so the *E* isomer should predominate since reduction of 1,1-dibromo-2-phenylcyclopropane (34) gave monobromide 41 consisting mainly of the isomer with the phenyl group and the bromine atom *cis* to each other (Table 2). Therefore it is necessary to take into account both steric and electronic interactions to explain the composition of 33.

## EXPERIMENTAL

**General.** The apparatus employed have been described elsewhere.<sup>28</sup> Elemental analyses were carried out by Ilse Beetz Microanalytical Laboratory, 8640 Kronach, West Germany.

**Preparation of starting materials.** Tributyltin hydride was prepared as described by Kuivila and Beumel.<sup>10</sup> With the exception of 2,2-dibromo-1,3,3-trimethylcyclopropylmethanol (15) the preparation of the *gem*-dibromocyclopropanes 1–14 will be described elsewhere.<sup>29,30</sup>

15 was prepared in 53% yield from bromoform and 2,3-dimethyl-2-buten-1-ol<sup>31</sup> following the procedure of Kleveland, Skattebøl and Sydnes,<sup>29</sup> m.p. 84–84.5°C from hexane. Anal. C<sub>7</sub>H<sub>13</sub>Br<sub>2</sub>O: C, H. <sup>1</sup>H NMR (60 MHz, CCl<sub>4</sub>): δ 1.28 (3 H, s), 1.35 (6 H, s), 1.93 (1 H, broad s), 3.80 (2 H, broad s). IR (CCl<sub>4</sub>): 3620 (m), 1020 (m) cm<sup>-1</sup>.

**Reduction of *gem*-dibromocyclopropanes; general procedure.** The reaction was carried out under pure nitrogen. During 5 min 6.1 g (21 mmol) of tributyltin hydride in 10 ml of dry ether was added to a stirred cooled (ice) solution of 20 mmol of *gem*-dibromocyclopropane in 20 ml of dry ether. The reaction mixture was then stirred for 2–4 h at 20°C. The product was isolated by distillation.

According to this procedure the following compounds were prepared from the corresponding *gem*-dibromocyclopropanes.

***E*- and *Z*-2-Acetyl-1-bromo-2-methylcyclopropane (16),** b.p. 32°C/0.06 mmHg. <sup>1</sup>H NMR (60 MHz, CCl<sub>4</sub>): δ 0.8–1.35 (1 H, m), 1.44 and 1.57 (3 H, s), 1.5–2.0 (1 H, m), 2.19 and 2.21 (3 H, 2s), 2.88 and 3.33 (1 H, 2dd in a ratio of 35:65, *J* 5 and 8 Hz),<sup>32</sup> IR (film): 1705(s), 1010(s), 790(m) cm<sup>-1</sup>.<sup>32</sup>

***E*- and *Z*-2-Acetyl-1-bromo-*cis*-2,3-dimethylcyclopropane (17),** b.p. 44°C/0.85 mmHg. <sup>1</sup>H NMR (60 MHz, CCl<sub>4</sub>): δ 1.10 (3 H, d, *J* 6 Hz), 1.36 (3 H, s), 1.1–1.9 (1 H, m partly hidden by the singlet and doublet), 2.18 and 2.25 (3 H, 2s in a ratio of 90:10), 2.58 and 3.52 (1 H, 2d in a ratio of 10:90, *J* 5 and 7.5 Hz, respectively).<sup>32</sup> IR (film): 1697(s), 1355(m), 1272(s), 1166(s), 962(m), 835(m), 695(m) cm<sup>-1</sup>.<sup>32</sup>

***E*- and *Z*-1-Acetyl-7-bromobicyclo[4.1.0]heptane (18),** b.p. 83–85°C/0.97 mmHg. Anal. C<sub>8</sub>H<sub>13</sub>BrO: C, H. <sup>1</sup>H NMR (60 MHz, CCl<sub>4</sub>): δ 1.0–2.7 (9 H, m), 2.18 (3 H, s), 2.83 and 3.59 (1 H, 2d in a ratio of 16:84, *J* 4.5 and 8 Hz, respectively). IR (film): 1690(s), 1020(w),

675(w), 550(w) cm<sup>-1</sup>. The isomeric composition was confirmed by GLC (10% PEG 4000, 100–180°C).

***E*- and *Z*-2-Acetyl-1-bromo-2,3,3-trimethylcyclopropane (21),** b.p. 28°C/0.06 mmHg. Anal. C<sub>9</sub>H<sub>13</sub>BrO: C, H. <sup>1</sup>H NMR (60 MHz, CCl<sub>4</sub>): δ 1.05 (3 H, s), 1.18 and 1.23 (3 H, 2s in a ratio of 92:8), 2.15 and 2.20 (3 H, 2s in a ratio of 93:7), 2.71 and 3.71 (1 H, 2s in a ratio of 7:93). IR (film): 1690(s), 1360(m), 1255(m), 1104(m), 975(w), 740(w) cm<sup>-1</sup>.

***E*-1-Bromo-2-isobutyryl-2,3,3-trimethylcyclopropane (22),** b.p. 39–40°C/0.8 mmHg. Anal. C<sub>10</sub>H<sub>17</sub>BrO: C, H. <sup>1</sup>H NMR (60 MHz, CCl<sub>4</sub>): δ 0.98 (3 H, s), 1.00 (3 H, d, *J* 7 Hz), 1.02 (3 H, partly hidden d, *J* 7 Hz), 1.18 (3 H, s), 1.42 (3 H, s), 2.90 (1 H, heptet, *J* 7 Hz), 3.78 (1 H, s). IR (film): 1695(s), 1380(s), 1043(s), 1010(m), 980(m), 730(w) cm<sup>-1</sup>.

**Butyl *E*- and *Z*-2-bromo-1-methylcyclopropanecarboxylate (25),** b.p. 58–60°C/0.5 mmHg. Anal. C<sub>9</sub>H<sub>15</sub>BrO<sub>2</sub>: C, H. <sup>1</sup>H NMR (98 MHz, CCl<sub>4</sub>): δ 0.85–1.90 (9H, m), 1.38–1.46 (3 H, 2s partly hidden by the multiplet), 2.84 and 3.44 (1 H, 2dd in a ratio of 27:73, *J* 5 and 8 Hz for both), 4.03 and 4.09 (2H, 2t, *J* 6.5 Hz for both). The ratio of the isomers was confirmed by GLC (10% PEG 4000, 155°C).

**Ethyl *E*- and *Z*-2-bromo-*cis*-1,3-dimethylcyclopropanecarboxylate (26),** b.p. 49–50°C/0.55 mmHg. Anal. C<sub>8</sub>H<sub>13</sub>BrO<sub>2</sub>: C, H. <sup>1</sup>H NMR (98 MHz, CCl<sub>4</sub>): δ 1.11 (3 H, d, *J* 6.5 Hz), 1.24 (3 H, s), 1.24 (3 H, t, *J* 7 Hz), 1.66 (1 H, asymmetric m), 2.52 and 3.59 (1 H, 2d in a ratio of 1:9, *J* 5 and 8 Hz, respectively), 4.06 (2 H, q, *J* 7 Hz). IR (film): 1700(s), 1270(s), 1100(s), 1075(s), 1020(m), 665(m) cm<sup>-1</sup>.

***E*- and *Z*-2-Bromo-1-methylcyclopropylmethanol (27),** b.p. 87–88°C/17 mmHg. Anal. C<sub>6</sub>H<sub>9</sub>BrO: C, H. <sup>1</sup>H NMR (60 MHz, CCl<sub>4</sub>): δ 0.53–1.30 (2 H, m), 1.23 and 1.30 (3 H, 2s in a ratio of 2:3), 2.83 and 2.95 (1 H, 2dd, *J* 4.5 and 7.5 Hz for both), 3.30 (1 H, broad s), 3.40 and 3.65 (2 H, 2 AB-q in a ratio of 65:35, *J* 11.5 Hz). IR (film): 3350(s), 1300(m), 1065(m), 1045(s), 1030(s), 960(m) cm<sup>-1</sup>. The product was shown to be a 65:35 mixture of stereoisomers by GLC (20% SE 30, 120°C).

***E*- and *Z*-1-(2-Bromo-1-methylcyclopropyl)-ethanol (28),** b.p. 39–41°C/0.80 mmHg. Anal. C<sub>6</sub>H<sub>11</sub>BrO: C, H. The product consisted of two isomers in a ratio of 38:62 according to GLC analyses (20% SE 30, 120–170°C) and these were separated by preparative GLC (20% SE 30, 115°C).

The isomer with shorter retention time (formed in lower yield): <sup>1</sup>H NMR (60 MHz, CCl<sub>4</sub>): δ 0.61–1.20 (2 H, partly hidden m), 1.10 (3 H, s), 1.20 (3 H, d, *J* 6.5 Hz), 1.65 (1 H, broad s), 2.82 (1 H, dd, *J* 4.5 and 7.5 Hz), 3.62 (1 H, q, *J* 6.5 Hz). IR (film): 3440(m), 3050(w), 1308(s), 1265(s), 1110(s), 1077(s), 1048(s), 950(s), 920(m) cm<sup>-1</sup>.

The isomer with longer retention time (the predominant isomer): <sup>1</sup>H NMR (60 MHz, CCl<sub>4</sub>):

$\delta$  0.60 (1 H, dd,  $J$  4 and 6 Hz), 1.17 (1 H, mostly hidden dd), 1.21 (3 H, d,  $J$  6.5 Hz), 1.26 (3 H, s), 1.67 (1 H, broad s), 2.95 (1 H, dd,  $J$  4.5 and 7.5 Hz), 3.20 (1 H, q,  $J$  6.5 Hz). IR (film): 3350(s), 3040(w), 1300(s), 1210(m), 1110(s), 1070(s), 1038(m), 960(w), 930(s)  $\text{cm}^{-1}$ .

*E*- and *Z*-1-(2-Bromo-*cis*-1,3-dimethylcyclopropyl)ethanol (29), b.p. 48–49°C/0.35 mmHg. Anal.  $\text{C}_7\text{H}_{13}\text{BrO}$ : C, H.  $^1\text{H}$  NMR [60 MHz,  $\text{CCl}_4(2)$  + benzene (1)]:  $\delta$  0.84–1.30 (4 H, mostly hidden m), 1.03 (3 H, s), 1.16 (3 H, d,  $J$  6.5 Hz), 1.79 and 2.50 (1 H, 2d in a ratio of 9:1,  $J$  6.5 and 4 Hz, respectively), 2.00 (1 H, broad s), 3.17 and 3.53 (1 H, 2q in a ratio of 9:1,  $J$  6.5 Hz for both). IR (film): 3360(s), 1390(m), 1265(m), 1115(s), 1065(s), 1040(m), 950(s), 915(s), 815(m), 690(m)  $\text{cm}^{-1}$ . GLC analyses (20% SE 30, 110–130°C) confirmed that 29 was a 1:9 mixture of stereoisomers.

*E*- and *Z*-1-(7-Bromobicyclo[4.1.0]heptyl)ethanol (30), b.p. 65–66°C/0.05 mmHg. The product was not obtained pure enough for elemental analysis.  $^1\text{H}$  NMR (60 MHz,  $\text{CCl}_4$ ):  $\delta$  0.70–2.50 (13 H, complex m), 2.85 and 3.23 (1 H, 2d in a ratio of 35:65,  $J$  4.5 and 7.5 Hz, respectively), 3.28 and 3.73 (1 H, 2q in a ratio of 65:35,  $J$  7 Hz for both). IR (film): 3380 (m), 1460(m), 1380(m), 1260(m), 1115(m), 1018(w), 920(w)  $\text{cm}^{-1}$ . GLC analyses (20% SE 30, 135–155°C) confirmed the ratio of the isomers. However, the isomers were not obtained pure by preparative GLC (same conditions) due to partial decomposition.

*E*- and *Z*-2-Bromo-1,3,3-trimethylcyclopropylmethanol (31), b.p. 72°C/0.7 mmHg. Anal.  $\text{C}_7\text{H}_{13}\text{BrO}$ : C, H.  $^1\text{H}$  NMR (60 MHz,  $\text{CCl}_4$ ):  $\delta$  1.13, 1.18, 1.20 and 1.23 (9 H, 4s), 1.46 (1 H, broad s), 2.68 and 2.84 (1 H, 2s in a ratio of 37:63), 3.55 and 3.64 (2 H, an AB-q,  $J$  11 Hz, and a broad s, respectively). IR (film): 3360(s), 1390(m), 1265(m), 1040(s), 1020 (s, shoulder), 945(w), 723(w)  $\text{cm}^{-1}$ . The isomeric composition was confirmed by GLC analyses (20% SE 30, 120–140°C).

*Preparation of E*-2-bromo-1-methylcyclopropanecarboxylic acid (56).<sup>34</sup> A solution of chromium trioxide (3.5 g) in water (10 ml) and concentrated sulfuric acid (2.9 ml) was added during 30 min to a stirred solution of 3.3 g of the predominant isomer of 2-bromo-1-methylcyclopropylmethanol (27) in acetone (15 ml) at 5°C. After stirring for a further 2½ h, the mixture was diluted with water to 150 ml and the product was extracted with ether; the combined organic fractions were dried with  $\text{MgSO}_4$ . Distillation afforded 3.0 g (84%) of 56, b.p. 78°C/0.05 mmHg (lit.<sup>32</sup> 161–163°C/45 mmHg). The spectral properties are in accordance with those published.<sup>32</sup>

*Oxidation of 1*-(2-bromo-1-methylcyclopropyl)ethanol (28). The oxidation was performed by a procedure analogous to that employed to prepare acid 56. A 3:2 isomeric mixture (according to GLC analyses) of 28 was used and distillation afforded a 93% yield of a mixture of the

*E* and *Z* isomers of 2-acetyl-1-bromo-2-methylcyclopropane (16). The NMR spectrum of the latter isomeric mixture disclosed an *E/Z* ratio of 58:42.

*Oxidation of 2-bromo-1,3,3-trimethylcyclopropylmethanol* (31). A 3:1 (from NMR) isomeric mixture of 31 was oxidized to the corresponding acid by the procedure employed to prepare 56. The reaction mixture was worked up in the usual way. Distillation afforded 2-bromo-1,3,3-trimethylcyclopropanecarboxylic acid in a yield of 80% as a 3:2:1 (from NMR) mixture of the *E* and *Z* isomers, b.p. 66°C/0.03 mmHg, m.p. 52–63°C.  $^1\text{H}$  NMR (60 MHz,  $\text{CCl}_4$ ):  $\delta$  1.15–1.60 (9 H, partly overlapping singlets), 2.84 and 3.72 (1 H, 2s in a ratio of 1:3.2), 9.55 (1 H, broad s). IR ( $\text{CCl}_4$ ): 3600–2400 (m), 1695 (s), 1015 (w), 920 (w)  $\text{cm}^{-1}$ .

*Reduction of 7,7-dibromo-4-isopropenyl-1-methylbicyclo[4.1.0]heptan-2-one* (4) with BTH. The reduction was performed following the general procedure to give a 90% yield of an 8:23:69 mixture of three monobromo derivatives according to GLC analyses (20% SE 30, 150–175°C) and spectroscopic examinations, b.p. 68°C/0.05 mmHg. The purity of the mixture was low due to contamination of tributyltin bromide. The three products were separated by preparative GLC (20% SE 30, 170°C).

20 (shortest retention time): Anal.  $\text{C}_{11}\text{H}_{15}\text{BrO}$ : C, H. IR ( $\text{CCl}_4$ ): 2960(s), 2890(w), 1705(s), 1390(w), 1375(w), 1342(m), 1298(m), 1250(m), 870(s), 700(m)  $\text{cm}^{-1}$ .

19 (the isomer formed in lower yield): Anal.  $\text{C}_{11}\text{H}_{15}\text{BrO}$ : C, H.  $^1\text{H}$  NMR (60 MHz,  $\text{CCl}_4$ ):  $\delta$  1.15–2.95 (6 H, partly hidden m), 1.21 (3 H, s), 1.80 (3 H, broad s), 3.22 (1 H, d,  $J$  7.5 Hz), 4.62–4.95 (2 H, m). IR (film): 3085(w), 1700(s), 1645(m), 1450(m), 1380(m), 1330(m), 1108(m), 910(s), 870(m)  $\text{cm}^{-1}$ .

19 (the predominant isomer, longest retention time): Anal.  $\text{C}_{11}\text{H}_{15}\text{BrO}$ : C, H.  $^1\text{H}$  NMR (60 MHz,  $\text{CCl}_4$ ):  $\delta$  1.33 (3 H, s), 1.55–2.66 (6 H, a partly hidden m), 1.77 (3 H, broad s), 3.47 (1 H, d,  $J$  4 Hz), 4.68–4.90 (2 H, m). IR (film): 3080(m), 3040(m), 1690(s), 1645(m), 1115(m), 995(m), 973(m), 900(s), 795(m)  $\text{cm}^{-1}$ .

*Reduction of ethyl 2,2-dibromo-1-phenylcyclopropanecarboxylate* (32) with BTH. Dibromide 32 was reduced in the usual way to give an isomeric mixture (35:65) of ethyl 2-bromo-1-phenylcyclopropanecarboxylate (33) according to GLC analyses (10% PEG 4000, 160–180°C). Spinning band distillation afforded monobromide 33, b.p. 80–82°C/0.05 mmHg, contaminated with appreciable amounts of tributyltin bromide. Both isomers were isolated pure by preparative GLC (10% PEG 4000, 190°C).

The isomer with shorter retention time (less abundant):  $^1\text{H}$  NMR (98 MHz,  $\text{CCl}_4$ ):  $\delta$  1.18 (3 H, t,  $J$  7.5 Hz), 1.64 (1 H, t,  $J$  5.5 Hz), 2.17 (1 H, dd,  $J$  5.5 and 7.5 Hz), 3.72 (1 H, dd,  $J$  5.5 and 7.5 Hz), 4.09 (2 H, q,  $J$  7.5 Hz), 7.30 (5 H, broad s). IR (film): 3040(w), 1705(s), 1598(w), 1497(m), 695(s)  $\text{cm}^{-1}$ .

The isomer with longer retention time (more abundant):  $^1\text{H}$  NMR (60 MHz,  $\text{CCl}_4$ ):  $\delta$  1.22 (3 H, t,  $J$  7.5 Hz), 1.62 (1 H, dd,  $J$  5.5 and 7.5 Hz), 2.10 (1 H, t,  $J$  5.5 Hz), 3.31 (1 H, dd,  $J$  5.5 and 7.5 Hz), 4.14 (2 H, roughly a double q,  $J$  7.5 Hz), 7.30 (5 H, m). IR ( $\text{CCl}_4$ ): 3035(w), 3010(w), 1730(s), 1602(w), 1500(m), 865(s), 700(s)  $\text{cm}^{-1}$ . Anal.  $\text{C}_{12}\text{H}_{13}\text{BrO}_2$  (mixture of isomers): C, H.

**Preparation of alkyl-substituted gem-dibromocyclopropanes.** 1,1-Dibromo-2-phenylcyclopropane (34), 1,1-dibromo-2-methyl-2-vinylcyclopropane (35), 1,1-dibromo-2-isopropenyl-2-methylcyclopropane (36) and 9,9-dibromobicyclo[6.1.0]nonane (38) were synthesized as described in the literature.<sup>35,36</sup>

1,1-Dibromo-2-ethyl-2,3,3-trimethylcyclopropane (40) was prepared from 2,3-dimethyl-2-pentene in 75% yield under two-phase conditions, b.p. 38°C/0.9 mmHg. Anal.  $\text{C}_9\text{H}_{14}\text{Br}_2$ : C, H.  $^1\text{H}$  NMR (60 MHz,  $\text{CCl}_4$ ):  $\delta$  1.02 (3 H, roughly a t,  $J$  6.5 Hz), 1.21 (3 H, s), 1.25 (3 H, s), 1.27 (3 H, s), 1.63 (2 H, roughly a q,  $J$  6.5 Hz). IR (film): 790(m)  $\text{cm}^{-1}$ .

**Reduction of alkyl- and phenyl-substituted gem-dibromocyclopropanes** with BTH were performed according to the general procedure. The following compounds were prepared.

**1-Bromo-2-phenylcyclopropane (41)**, b.p. 53–55°C/0.2 mmHg (lit.<sup>7</sup> 48–50°C/0.15 mmHg). According to GLC analyses (20% SE 30, 165–180°C) 41 is a 35:65 mixture of stereoisomers. The isomer formed in lower yield was separated by preparative GLC (same conditions) and examined by  $^1\text{H}$  NMR spectroscopy (60 MHz,  $\text{CCl}_4$ ). The spectrum was almost identical to that of the *anti* isomer but much different from that of the *syn* isomer of 1-chloro-2-phenylcyclopropane.<sup>37</sup>

**1-Bromo-2-methyl-2-vinylcyclopropane (42)**, b.p. 59–61°C/60 mmHg. Anal.  $\text{C}_6\text{H}_8\text{Br}$ : C, H. GLC (10% PEG 4000, 100°C) revealed that 42 was a 42:58 mixture of stereoisomers which were separated by preparative GLC (same conditions).

The isomer formed in lower yield (shorter retention time):  $^1\text{H}$  NMR (60 MHz,  $\text{CCl}_4$ ):  $\delta$  0.88 (1 H, dd,  $J$  4.5 and 6 Hz), 1.30 (1 H, a partly hidden dd), 1.36 (3 H, s), 2.92 (1 H, dd,  $J$  4.5 and 7.5 Hz), 4.75–5.25 (2 H, m), 5.30–5.83 (1 H, m, X part of an ABX system). IR (film): 3080(m), 1632(s), 1030(m), 990(s), 905(s)  $\text{cm}^{-1}$ .

The predominant isomer:  $^1\text{H}$  NMR (60 MHz,  $\text{CCl}_4$ ):  $\delta$  0.88–1.56 (2 H, a partly hidden m), 1.24 (3 H s), 2.92 (1 H, dd,  $J$  5 and 7.5 Hz), 3.64–5.90 (3 H, m). IR (film): 3080(m), 1636(s), 990(m), 905(m)  $\text{cm}^{-1}$ .

**1-Bromo-2-isopropenyl-2-methylcyclopropane (43)** as a mixture of isomers in a ratio of 57:43 as determined by GLC (10% PEG 4000, 112°C), b.p. 56–57°C/27 mmHg. The isomers were separated by preparative GLC (same conditions). Their  $^1\text{H}$  NMR spectra are in accordance with those published, the predominant isomer

being the same in this case as in the reaction carried out by de Wolf and co-workers.<sup>38</sup>

**9-Bromobicyclo[6.1.0]nonane (45)**, b.p. 44–46°C/0.18 mmHg (lit.<sup>7</sup> 40–42°C/0.13 mmHg). GLC (20% SE 30, 175°C) disclosed the presence of two stereoisomers in a ratio of 13:87; these were separated by preparative GLC (same conditions) and examined by NMR spectroscopy.  $^1\text{H}$  NMR (60 MHz,  $\text{CCl}_4$ , predominant isomer with longer retention time):  $\delta$  0.63–2.34 (14 H, m), 3.15 (1 H, t,  $J$  7.5 Hz). The  $^1\text{H}$  NMR spectrum of the isomer formed in lower yield is identical to that published by Osborn and co-workers.<sup>39</sup>

**1-Bromo-2-ethyl-2,3,3-trimethylcyclopropane (47)**, b.p. 64°C/24 mmHg. Anal.  $\text{C}_9\text{H}_{16}\text{Br}$ : C, H.  $^1\text{H}$  NMR (60 MHz,  $\text{CCl}_4$ ):  $\delta$  0.77–2.00 (14 H, m), 2.64 and 2.68 (1 H, 2s in a ratio of 19:81, respectively). IR (film): 868(w), 795(w), 712(w)  $\text{cm}^{-1}$ .

**Preparation of anti-1-bromo-2-isopropenyl-2-methylcyclopropane (43a).** The reaction was carried out under pure nitrogen.

Triphenylphosphonium iodide, 8.1 g (20 mmol), was added in portions to a mixture of 12.5 ml of a 1.6 M solution of butyl lithium (20 mmol) and 30 ml of dry ether. This mixture was then stirred at room temperature for 3 h, after which a solution of 3.5 g (20 mmol) of *E*-2-acetyl-1-bromo-2-methylcyclopropane<sup>40</sup> in 30 ml of dry ether was added dropwise. A white precipitate formed immediately. The mixture was then refluxed for 24 h, cooled, and filtered by suction. The residue was washed with ether and the combined filtrates were washed with water until neutral; the ethereal solution was then dried ( $\text{MgSO}_4$ ). Distillation gave 1.3 g of a 1:6 mixture of starting material and 43a which were separated by preparative GLC (20% SE 30, 90°C). The spectral properties (IR and NMR) of 43a were identical with those of the isomer formed in higher yield when 36 was reduced with BTH.

**Acknowledgement.** The author wishes to thank Professor L. Skattebøl for valuable discussions.

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Received July 12, 1977.