

## Chemistry of *gem*-Dihalocyclopropanes. XI. Reactions of Dihalocarbenes with Allylic Alcohols

KARSTEN KLEVELAND, LARS SKATTEBØL and LEIV K. SYDNES

Department of Chemistry, University of Oslo, Oslo 3, Norway

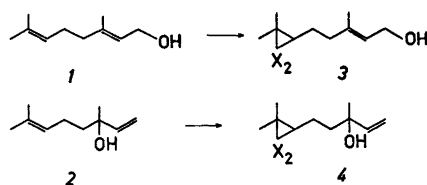
Reactions of dichloro- or dibromocarbene, generated by the phase transfer method, with a number of allylic alcohols resulted in formation of the corresponding dihalocyclopropane derivatives in variable yields. The addition to linalool occurred exclusively at the trisubstituted double bond in excellent yields. In two examples insertion at the O—H bond was an important reaction. The results indicate no electronic interaction between the hydroxyl group and the carbene leading to stereochemical consequences.

Addition of dihalocarbene to allylic alcohols has been reported by several groups. Seyferth and Mai<sup>1</sup> studied particularly cyclic alcohols using phenyl bromodichloromethyl mercury as the source of dichlorocarbene; *trans* stereochemistry was observed in all cases, indicating the lack of any directing effect of the hydroxyl group. The reaction of bicyclo [6.4.0]dodec-1(8)-en-12-ol with dibromocarbene, generated from bromoform and potassium *t*-butoxide, has been reported,<sup>2</sup> but the cycloaddition product was not isolated. A number of open chain alcohols have also been studied. Allyl alcohol and dichlorocarbene, generated as above, gave products derived from reaction at the O—H bond only.<sup>2,3</sup> Alkyl-substituted allylic alcohols, however, reacted with dichlorocarbene,<sup>1,4</sup> dibromocarbene<sup>5</sup> and chlorofluorocarbene<sup>6</sup> by addition to the double bond. A preferred stereochemistry was not reported in any of the additions, but a high degree of regioselectivity was observed<sup>4</sup> in the addition of dichlorocarbene to (*E*)-3-methyl-2,6-heptadiene-1-ol, under phase transfer conditions.<sup>7</sup>

In the present paper we want to report on additions of dihalocarbenes to a number of

allylic alcohols which provided examples of both regio- and stereoselectivity. The carbenes were generated by the phase transfer method and in some cases the yields were excellent.

The work was initiated after we had observed a surprising difference in behaviour of geraniol (1) and linalool (2) towards dichlorocarbene; the former was considerably less reactive and a low yield of a high-boiling liquid consisting of at least six components was obtained. Attempts to separate them resulted in partial decomposition, but the main component was most probably compound 3. On the other hand, linalool reacted rapidly and regioselectively with dichlorocarbene to yield 89 % of compound 4 (X=Cl); the corresponding dibromo derivative 4 (X=Br) was obtained in 93 % yield under conditions generating dibromocarbene (Scheme 1).



Scheme 1.

The two terpene isomers differ structurally in the allylic hydroxyl function, and apparently the primary allylic hydroxyl group not only competes with the double bonds for dihalocarbene, but it also seemed to have a retarding effect on the rate of addition. It was therefore of interest to study the behaviour of a variety of allylic alcohols under similar conditions.

Table 1. Reactions of allylic alcohols with dihalocarbenes.

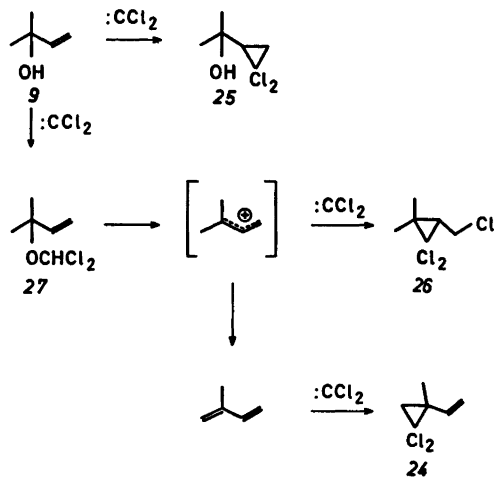
Starting material	Product	Yield %
5	13 <sup>a</sup>	R = R <sup>1</sup> = R <sup>3</sup> = R <sup>4</sup> = H; R <sup>2</sup> = CH <sub>3</sub> ; X = Cl 70 <sup>b</sup>
5	14	R = R <sup>1</sup> = R <sup>3</sup> = R <sup>4</sup> = H; R <sup>2</sup> = CH <sub>3</sub> ; X = Br 34 <sup>c</sup>
6	15 <sup>d</sup>	R = R <sup>1</sup> = R <sup>3</sup> = H; R <sup>2</sup> = R <sup>4</sup> = CH <sub>3</sub> ; H = Cl 75
6	16 <sup>e</sup>	R = R <sup>1</sup> = R <sup>3</sup> = H; R <sup>2</sup> = R <sup>4</sup> = CH <sub>3</sub> ; X = Br 62
7	17 <sup>f</sup>	R <sup>1</sup> = R <sup>3</sup> = R <sup>4</sup> = H; R = R <sup>2</sup> = CH <sub>3</sub> ; X = Br 45
8	18 <sup>g</sup>	R = R <sup>1</sup> = R <sup>3</sup> = CH <sub>3</sub> ; R <sup>2</sup> = R <sup>4</sup> = H; X = Cl 90
8	19 <sup>h</sup>	R = R <sup>1</sup> = R <sup>3</sup> = CH <sub>3</sub> ; R <sup>2</sup> = R <sup>4</sup> = H; X = Br 74
9	i	R = R <sup>1</sup> = R <sup>3</sup> = H; R <sup>2</sup> = R <sup>4</sup> = CH <sub>3</sub> ; X = Cl
10	20	R = R <sup>1</sup> = H; R <sup>2</sup> = R <sup>3</sup> = R <sup>4</sup> = CH <sub>3</sub> ; X = Cl 69
11	21	R = R <sup>1</sup> = R <sup>3</sup> = R <sup>4</sup> = CH <sub>3</sub> ; R <sup>2</sup> = H; X = Cl 88
11	22	R = R <sup>1</sup> = R <sup>3</sup> = R <sup>4</sup> = CH <sub>3</sub> ; R <sup>2</sup> = H; X = Br 88
12	28	R = R <sup>1</sup> = R <sup>3</sup> = CH <sub>3</sub> ; R <sup>2</sup> = R <sup>4</sup> = H; X = Cl 81

<sup>a</sup> A 4:1 ratio of 9 and 23 (2,2-dichloro-1-methyl-1-dichloromethoxymethylcyclopropane) was formed in 20% yield. <sup>b</sup> A 3-fold excess of CHCl<sub>3</sub>/NaOH and 72 h reaction time. <sup>c</sup> Recovered starting material 51%. <sup>d</sup> Ratio of diastereomers 48:52. <sup>e</sup> Ratio of diastereomers 45:55. <sup>f</sup> A mixture of *E* and *Z* isomers in a ratio of 1:1; 3-fold excess of CHBr<sub>3</sub>/NaOH. <sup>g</sup> Ratio of diastereomers 90:10 determined by GC. <sup>h</sup> Ratio of diastereomers 81:19 determined by NMR. <sup>i</sup> Six products besides carbon monoxide were formed. Compounds 24, 25 and 26 (Scheme 2) were identified.

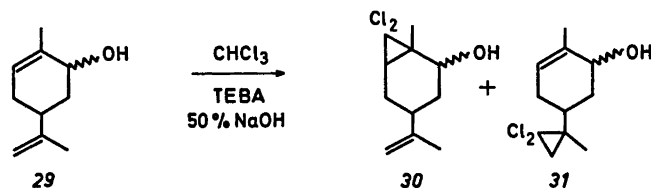
The allylic alcohols (5–12) used in this study were either commercial samples or prepared according to known procedures. Usually a two-fold excess of haloform, a three-fold excess of base and 16 h reaction time were used to ensure completion of the reactions at room temperature. As catalysts either benzyltriethylammonium chloride (TEBA) or tributylamine were employed; however, the latter was in all cases inferior and the results summarized in Table 1 are those from reactions with TEBA as catalyst.

Insertion at the O–H bond is an observable reaction in the case of the primary alcohol 5, but methyl substitution at the double bond renders this the preferred site of attack by the carbene in contrast to allylic alcohol itself.<sup>3</sup> However, the products from the reaction of alcohol 9 with dichlorocarbene strongly suggest that also in this case insertion into the O–H bond occurred initially. Carbon monoxide escaped during the reaction and a mixture of six compounds was formed in low yield. These were separated by preparative GC, and on the

basis of spectroscopic evidence and comparison with authentic material we were able to ascertain the structures of the three main components 24, 25 and 26, representing 81% of the mixture. The structures of the three



Scheme 2.



Scheme 3.

minor components are uncertain. The results are rationalized in Scheme 2. We suggest that fragmentation of a carbene intermediate derived from the insertion product 27 takes place; reactions of the resulting carbenium ion provides the necessary substrates for formation of the observed dichlorocarbene addition products. Other results which support the proposed mechanism have been reported.<sup>8</sup>

With the other alcohols of Table I addition to the double bond was the exclusive reaction. It appears that the hydroxyl function deactivates the double bond of allylic alcohols towards electrophilic reagents and that alkyl substituents are a prerequisite for a reasonable yield of cycloaddition products. This is further supported by the results from the reaction of dichlorocarbene with carvol (29); almost 50% of the product derives from addition to the disubstituted exocyclic double bond (Scheme 3).

The formation of a stereoisomeric mixture of the cyclopropanes obtained from dibromocarbene addition to the alcohol 7 deserves further comment. The apparent lack of stereospecificity is not compatible with a dihalocarbene addition; however, recovered starting material 7 consisted of a mixture of *E* and *Z* isomers in a ratio of 2:1, not significantly different from that observed for the product. Clearly a fast base-catalyzed isomerization of the alcohol 7 had occurred prior to the carbene addition. There are only a few reported examples of base-induced isomerization of allylic alcohols<sup>9</sup> and none of them are under phase transfer conditions. Abstraction of a proton at either of the methyl groups would lead to an allylic carbanion that could isomerize. We cannot distinguish between the two mechanisms but it is interesting that the structurally isomeric alcohols 2-ethyl-2-propen-1-ol and 2-methyl-3-buten-1-ol were not detected in the product.

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The double bonds of both compounds 6 and 8 are prochiral; *e.g.* addition of dihalocarbene could produce mixtures of diastereomers which indeed occurred in both cases. From the reaction of either dichloro- or dibromocarbene with 6 almost equal amounts of two diastereomers were obtained, in agreement with the observation of Santelli and Bertrand;<sup>5</sup> however, the corresponding reactions with 8 exhibited considerable stereoselectivity as shown by the 9:1 and 4:1 ratios of diastereomers obtained from addition of dichlorocarbene and dibromocarbene, respectively, in contrast to the lack of selectivity reported by the above authors<sup>5</sup> and others.<sup>1,4</sup> The question arises whether the selectivity originates in steric factors or a guiding effect of the hydroxyl group. The latter is clearly not important in the case of dichlorocarbene addition to cyclic allylic alcohols,<sup>1</sup> but in other carbenoid additions<sup>10</sup> and in epoxidation reactions<sup>11</sup> it has been observed.

On the basis of molecular models it seems plausible that the alcohol 8 should prefer the conformation depicted in Fig. 1. Assuming a ground state conformational control of products the preferred direction of dihalocarbene addition to the double bond of this conformer should indicate which effects are important in determining the stereochemistry. The structure of the most abundant dia-

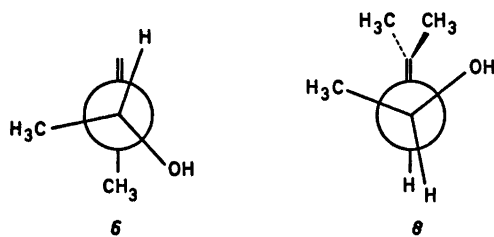


Fig. 1. Assumed preferred conformations of compounds 6 and 8.

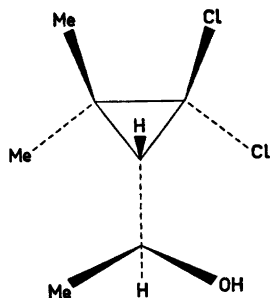


Fig. 2. Perspective drawing of the structure of 1-(2,2-dichloro-3,3-dimethylcyclopropyl)ethanol 18.<sup>12</sup>

stereomer of 18 was determined<sup>12</sup> by X-ray crystallography (Fig. 2). In the crystal state the chlorine atoms and the hydroxyl group are on the same side of the plane comprising the methine carbon and bisecting the cyclopropane ring. This configuration indicates that addition of dichlorocarbene to the double bond has occurred preferably from the least sterically hindered side but also in close proximity to the hydroxyl group; hence, from this result no conclusion can be drawn about the factors determining the observed selectivity. However, from the alcohol 6 practically equal amounts of the diastereomers 15 were obtained and by considering in the same way preferred addition to the most plausible conformers (Fig. 1) it seems that the effect of the hydroxyl group is only steric.

All evidence so far available on the addition of dichloro- or dibromocarbene to allylic alcohols suggests that the hydroxyl group renders the double bond less reactive and further that the interaction is negligible between the hydroxyl oxygen and the approaching carbene in reference to stereochemical consequences. However, the difference in reactivity between geraniol (1) and linalool (2) towards dihalocarbene remains unexplained.

## EXPERIMENTAL

**General.** Most of the spectral and gas chromatographic equipment used has been described previously.<sup>13</sup> <sup>13</sup>C NMR spectra were obtained on a JEOL FX 60. <sup>1</sup>H NMR were recorded at 60 MHz when not stated otherwise. Elemental analyses were carried out by Ilse Beetz Microanalytical Laboratory, 8640 Kronach, West Germany.

**Allylic alcohols.** Geraniol (1), linalool (2), 2-methyl-2-propen-1-ol (5), 2-methyl-3-buten-2-ol (9) and carvol (29) were obtained commercially. The following alcohols were prepared according to the literature: 3-methyl-3-buten-2-ol (6),<sup>18</sup> 2,3-dimethyl-3-buten-2-ol (10),<sup>16</sup> 2,4-dimethyl-3-penten-2-ol (11)<sup>17</sup> and 2,3-dimethyl-2-buten-1-ol (12);<sup>14</sup> in the case of compound 10 the yield was increased to 82 % by using methyllithium.

(*E*)-2-Methyl-2-buten-1-ol (7) was prepared in 95 % yield by the lithium aluminium hydride reduction of tiglaldehyde at -80 °C for 5 min and 0 °C for 15 min, b.p. 57–58 °C/23 mmHg,  $n_D^{25}$  1.4420 (lit.<sup>14</sup> b.p. 74 °C/60 mmHg,  $n_D^{20}$  1.4421). The IR and NMR spectra were in accordance with those published.<sup>14,15</sup>

5-(2,2-Dichloro-3,3-dimethylcyclopropyl)-3-methyl-1-penten-3-ol (4, X=Cl). A mixture of 30.8 g (0.20 mol) of linalool (2), 35.8 g (0.30 mol) of CHCl<sub>3</sub>, 32.0 g (0.40 mol) of 50 % aq. NaOH, and 0.4 g triethylbenzylammonium chloride (TEBA) was stirred vigorously for 16 h at 20 °C. Water was added and the product extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic phases were washed with water and dried (MgSO<sub>4</sub>). Evaporation of the solvent left a pale yellow residue which distilled at 98 °C/0.01 mmHg through a short path apparatus to yield 42.0 g (89 %) of 4. Anal. C<sub>11</sub>H<sub>18</sub>Cl<sub>2</sub>O: C, H. <sup>1</sup>H NMR (CCl<sub>4</sub>): δ 1.17 (3 H, s), 1.27 (3 H, s), 1.35 (3 H, s), 1.0–1.7 (5 H, m), 1.70 (1 H, s), 4.7–6.1 (3 H, vinyl m). IR (film): 3400 (s), 1630 (w), 825 (s) cm<sup>-1</sup>.

5-(2,2-Dibromo-3,3-dimethylcyclopropyl)-3-methyl-1-penten-3-ol (4, X=Br), m.p. 41–45 °C (from pentane). Anal. C<sub>11</sub>H<sub>18</sub>Br<sub>2</sub>O: C, H. <sup>1</sup>H NMR (CCl<sub>4</sub>): δ 1.19 (3 H, s), 1.28 (3 H, s), 1.38 (3 H, s), 1.1–1.7 (5 H, m), 1.66 (1 H, s), 4.8–6.1 (3 H, vinyl m). IR (film) 3400 (s), 750 (s) cm<sup>-1</sup>.

2,2-Dichloro-1-methylcyclopropylmethanol (13) and 2,2-dichloro-1-methyl-1-dichloromethoxymethylcyclopropane (23). The product consisted of a mixture that was separated by prep. GC (10 % QF1, 155 °C):

13 (shorter retention time) b.p. 84–86 °C/9 mmHg,  $n_D^{21}$  1.4907. Anal. C<sub>6</sub>H<sub>9</sub>Cl<sub>2</sub>O: C, H. <sup>1</sup>H NMR (98 MHz, CCl<sub>4</sub>): δ 1.23 (1 H, d, *J* 7 Hz), 1.39 (1 H, d, *J* 7 Hz), 1.45 (3 H, s), 1.63 (1 H, broad s), 3.61 (1 H, d, *J* 12 Hz), 3.73 (1 H, d, *J* 12 Hz). IR (film): 3320 (s), 1035 (s), 760 (s) cm<sup>-1</sup>.

23 b.p. 88 °C/9 mmHg,  $n_D^{24}$  1.4720. <sup>1</sup>H NMR (98 MHz, CCl<sub>4</sub>): δ 1.32 (1 H, d, *J* 7.5 Hz), 1.45 (3 H, s), 1.51 (1 H, d, *J* 7.5 Hz), 4.14 (1 H, d, *J* 11.5 Hz), 4.40 (1 H, d, *J* 11.5 Hz), 8.04 (1 H, s). <sup>13</sup>C NMR (15.0 MHz, CCl<sub>4</sub>): δ 18.5, 29.2, 30.9, 64.5, 67.2, 158.9. IR (film): 1690 (s), 1460 (s), 1165 (s), 1050 (s), 968 (m), 764 (s) cm<sup>-1</sup>. No elemental analysis was obtained due to instability.

2,2-Dibromo-1-methylcyclopropylmethanol (14), b.p. 60–61 °C/0.9 mmHg, m.p. 66.5 °C (from pentane). Anal. C<sub>6</sub>H<sub>9</sub>Br<sub>2</sub>O: C, H. <sup>1</sup>H NMR

(benzene):  $\delta$  1.08 (1 H, d,  $J$  7.5 Hz), 1.24 (1 H, d,  $J$  5 Hz), 1.32 (3 H, s), 2.57 (1 H, s), 3.52 (1 H, s). IR (film): 3390 (s), 1040 (s), 685 (s)  $\text{cm}^{-1}$ .

*1-(2,2-Dichloro-1-methylcyclopropyl)ethanol* (15), b.p. 86–90°C/15 mmHg. Anal.  $\text{C}_8\text{H}_{10}\text{Cl}_2\text{O}$ : C, H. GC (10% PEG 4000, 160°C) revealed the presence of two diastereomers in a ratio of 48:52. They were separated by prep. GC (same column):

a. (shorter retention time) m.p. 39–40°C (from pentane).  $^1\text{H}$  NMR ( $\text{CCl}_4$ ):  $\delta$  1.1–1.3 (8 H, overlapping s and d), 2.50 (1 H, broad s), 3.67 (1 H, q,  $J$  6.5 Hz). IR (film): 3570 (w), 3400 (s), 750 (s)  $\text{cm}^{-1}$ .

b.  $^1\text{H}$  NMR ( $\text{CCl}_4$ ):  $\delta$  1.1–1.5 (8 H, overlapping s and d), 2.77 (1 H, broad s), 3.60 (1 H, q,  $J$  6.5 Hz). IR (film): 3570 (w), 3350 (s), 750 (s)  $\text{cm}^{-1}$ .

*1-(2,2-Dibromo-1-methylcyclopropyl)ethanol* (16), b.p. 51–52°C/0.1 mmHg,  $n_D^{21}$  1.5422. Anal.  $\text{C}_8\text{H}_{10}\text{Br}_2\text{O}$ : C, H.  $^1\text{H}$  NMR ( $\text{CCl}_4$ ):  $\delta$  1.10–1.95 (8 H, complex m), 2.42 (1 H, s), 3.41–3.91 (1 H, m). IR (film): 3580 (m), 3410 (s), 1020 (s), 1010 (s), 690 (s)  $\text{cm}^{-1}$ . According to GC (10% PEG 4000, 145°C) the product consists of a mixture of diastereomers in a ratio of 45:55.

(*E*)- and (*Z*)-2,2-Dibromo-1,2-dimethylcyclopropylmethanol (17). Distillation of the reaction mixture gave two main fractions:

a. (10%), b.p. 45°C/16 mmHg, of a 2:1 mixture of (*E*)- and (*Z*)-7.

b. (45%), b.p. 50–52°C/0.05 mmHg, of a 1:1 mixture of (*E*) and (*Z*)-17. Found: C 28.45; H 3.95. Calc. for  $\text{C}_8\text{H}_{18}\text{Br}_2\text{O}$ : C 27.93; H 3.91.  $^1\text{H}$  NMR ( $\text{CCl}_4$ ):  $\delta$  1.15 (3 H, d,  $J$  5 Hz), 1.18 (3 H, d,  $J$  5.5 Hz), 1.25 (3 H, s), 1.33 (3 H, s), 1.25–1.80 (2 H, complex m), 3.10 (2 H, broad s), 3.55 (1 H, d,  $J$  10.5 Hz), 3.62 (1 H, d,  $J$  12 Hz), 3.66 (1 H, d,  $J$  10.5 Hz), 3.72 (1 H, d,  $J$  12 Hz). IR (film): 3575 (w), 3380 (m), 1025 (s), 796 (s), 767 (s)  $\text{cm}^{-1}$ .

*1-(2,2-Dichloro-3,3-dimethylcyclopropyl)ethanol* (18). The product was shown by GC (10% PEG 4000, 150°C) to consist of two diastereomers in a ratio of 90:10.

a. The major isomer was pure by recryst. from pentane, m.p. 71–72°C (lit.<sup>1</sup> 73–73.5°C).

b. The minor isomer was obtained pure by prep. GC (same column as above).  $^1\text{H}$  NMR ( $\text{CCl}_4$ ):  $\delta$  1.16 (1 H, d,  $J$  9 Hz), 1.32 (3 H, s), 1.36 (3 H, d,  $J$  6 Hz), 1.38 (3 H, s), 1.97 (1 H, s), 3.64 (1 H, d q,  $J$  9,  $J$  6 Hz). IR (film): 3580 (w), 3320 (s), 805 (s)  $\text{cm}^{-1}$ . The above reaction was followed by GC and shown to be complete after 3.5 h. In two separate experiments a 10% excess of  $\text{NaOH}/\text{CHCl}_3$  yielded 44% and a 50% excess gave 64% of the adducts 18; with 50% excess but without the catalysts TEBA 19% of 18 was isolated. In all these experiments starting material was recovered.

*1-(2,2-Dibromo-3,3-dimethylcyclopropyl)ethanol* (19). The product was distilled at bath temperature <100°C/0.01 mmHg (lit.<sup>4</sup> b.p. 80°C/0.15 mmHg) as a 81:19 mixture of diastereomers *a* and *b*. The distillate crystallized and separation of the diastereomers was achieved by recrystallization and chromatography on silica gel.

a. M.p. 84–85°C (from pentane).  $^1\text{H}$  NMR ( $\text{CCl}_4$ ):  $\delta$  1.23 (3 H, d,  $J$  6 Hz), 1.25 (3 H, s), 1.37 (1 H, d,  $J$  9 Hz), 1.38 (3 H, s), 2.42 (1 H, s), 3.61 (1 H, d q,  $J$  9,  $J$  6 Hz). IR ( $\text{CCl}_4$ ): 3610 (s), 3470 (m), 1095 (s)  $\text{cm}^{-1}$ .

b. M.p. 63–65°C (from pentane).  $^1\text{H}$  NMR ( $\text{CCl}_4$ ):  $\delta$  1.24 (1 H, d,  $J$  9 Hz), 1.35 (3 H, s), 1.40 (3 H, d,  $J$  6 Hz), 1.45 (3 H, s), 3.53 (1 H, d q,  $J$  9,  $J$  6 Hz). IR ( $\text{CCl}_4$ ): 3620 (s), 3480 (m), 1100 (s)  $\text{cm}^{-1}$ .

*2-(2,2-Dichloro-1-methylcyclopropyl)propan-2-ol* (20), b.p. 78–81°C/17 mmHg. Anal.  $\text{C}_8\text{H}_{14}\text{Cl}_2\text{O}$ : C, H.  $^1\text{H}$  NMR ( $\text{CCl}_4$ ):  $\delta$  1.00 (1 H, d,  $J$  7 Hz), 1.27 (3 H, s), 1.28 (3 H, s), 1.50 (3 H, s), 1.89 (1 H, broad s), 2.10 (1 H, d,  $J$  7 Hz). IR (film): 3580 (m), 3470 (m), 750 (s)  $\text{cm}^{-1}$ .

*2-(2,2-Dichloro-3,3-dimethylcyclopropyl)propan-2-ol* (21), b.p. 66–67°C/8 mmHg. Anal.  $\text{C}_8\text{H}_{14}\text{Cl}_2\text{O}$ : C, H.  $^1\text{H}$  NMR ( $\text{CCl}_4$ ):  $\delta$  1.12 (1 H, s), 1.26 (3 H, s), 1.37 (3 H, s), 1.47 (6 H, s), 1.75 (1 H, s). IR (film): 3580 (m), 3460 (m), 835 (s), 760 (s)  $\text{cm}^{-1}$ .

*2-(2,2-Dibromo-3,3-dimethylcyclopropyl)propan-2-ol* (22), b.p. 53°C/10<sup>-3</sup> mmHg, m.p. 22–23°C (from pentane). Anal.  $\text{C}_8\text{H}_{14}\text{Br}_2\text{O}$ : C, H.  $^1\text{H}$  NMR:  $\delta$  1.26 (4 H, ss), 1.42 (3 H, s), 1.50 (6 H, s), 1.84 (1 H, s). IR (film): 3580 (s), 3490 (m), 955 (s), 715 (s)  $\text{cm}^{-1}$ .

*Reaction of 2-methyl-3-buten-2-ol (9) with excess dichlorocarbene.* A mixture of 8.6 g (0.10 mol) of 9, 35.7 g (0.30 mol) of  $\text{CHCl}_3$ , 24.0 g (0.30 mol) of 50% aq.  $\text{NaOH}$  and 0.2 g of TEBA was stirred vigorously for 16 h at room temperature. The reaction mixture was worked up in the usual way. A sample of the gas evolved during the reaction was collected over  $\text{CCl}_4$  and characterized as CO (IR). The crude reaction mixture consisted of starting allyl alcohol (63%) and 6 products, according to GC (20% SE 30). The products were separated by prep. GC (same column): *a* (shortest retention time). 24% of the product was shown to be 1,1-dichloro-2-methyl-2-vinylcyclopropane (24) by comparison with an authentic sample.<sup>18</sup> *b*. 19%, 2-(2,2-dichlorocyclopropyl)propan-2-ol (25). Anal.  $\text{C}_8\text{H}_{10}\text{Cl}_2\text{O}$ : C, H.  $^1\text{H}$  NMR ( $\text{CCl}_4$ ):  $\delta$  1.23 (3 H, s), 1.48 (3 H, s), 1.5–1.8 (4 H, m). IR (film): 3590 (s), 3450 (s), 750 (s)  $\text{cm}^{-1}$ . *c*. 38%, 1,1-dichloro-2-chloromethyl-3,3-dimethylcyclopropane (26). Anal.  $\text{C}_8\text{H}_{10}\text{Cl}_3$ : C, H.  $^1\text{H}$  NMR ( $\text{CCl}_4$ ):  $\delta$  1.28 (3 H, s), 1.42 (3 H, s), 1.3–1.8 (1 H, m), 3.2–4.0 (2 H, m). IR (film): 2970 (s), 850 (s), 720 (s)  $\text{cm}^{-1}$ . The three remaining compounds, *d*, *e*, and *f* comprising 19% of the product were not obtained pure enough for identification.

*2,2-Dichloro-1,3,3-trimethylcyclopropylmethanol* (28), m.p. 75 °C (from hexane). Anal.  $C_8H_{12}Cl_2O$ : C, H.  $^1H$  NMR ( $CCl_4$ ):  $\delta$  1.24 (3 H, s), 1.30 (6 H, s), 2.61 (1 H, s), 3.72 (2 H, broad s). IR (KBr): 3250 (s), 1020 (s), 840 (s)  $cm^{-1}$ .

*Reaction of carvol (29) with dichlorocarbene.* A mixture of 7.6 g (50 mmol) of carvol, 6.0 g (50 mmol) of  $CHCl_3$ , 4.0 g (50 mmol) of 50 % aq. NaOH, and 0.2 g of TEBA was stirred vigorously for 16 h at room temperature. The reaction mixture was worked up in the usual way. Short path distillation gave 3.3 g (43 %) of carvol and 4.4 g (38 %) of a mixture of monoadducts, b.p. 102–106 °C/0.01 mmHg.  $^1H$  NMR ( $CCl_4$ ) (with approx. integrals):  $\delta$  1.0–2.2 (13 H, overlap, s and m), 3.7–4.1 (2 H, m) 4.66 (1 H, broad s), 5.45 (0.5 H, m). IR (film): 3340 (s), 1640 (m), 750 (m)  $cm^{-1}$ .

On the basis of the integrals of the NMR-resonances at  $\delta$  4.66 and 5.45 we concluded that the two monoadducts 30 and 31 are present in approximately equal amounts. Small amounts of diadducts m.p. 110–115 °C (pentane) could be isolated from the residue after distillation.

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## REFERENCES

- Seyferth, D. and Mai, V. A. *J. Am. Chem. Soc.* 92 (1970) 7412.
- Hirano, S., Hiyama, T. and Nozaki, H. *Tetrahedron* 32 (1976) 2381.
- Seyferth, D., Mai, V. A., Mui, J. Y. P. and Darragh, K. V. *J. Org. Chem.* 31 (1966) 4079.
- Hiyama, T., Tsukanaka, T. and Nozaki, H. *J. Am. Chem. Soc.* 96 (1974) 3713.
- Santelli, C. and Bertrand, M. *Bull. Soc. Chim. Fr.* (1974) 605.
- Chan, L. V. and Schlosser, M. *Synthesis* (1973) 112.
- Makosza, M. and Wawrzyniewicz, W. *Tetrahedron Lett.* (1969) 4659; Makosza, M. *Pure Appl. Chem.* 43 (1975) 439.
- Kirmse, W. *Carbene Chemistry*, Academic, New York 1971, p. 428; Tabushi, I. and Aoyama, Y. *J. Org. Chem.* 38 (1973) 3447; Stromquist, P., Radcliffe, M. and Weber, W. P. *Tetrahedron Lett.* (1973) 4523, and references therein.
- Cram, D. J. *Fundamentals of Carbanion Chemistry*, Academic, New York 1965, p. 193.
- Dauben, W. G. and Berezin, G. H. *J. Am. Chem. Soc.* 85 (1963) 468.
- Chautemps, P. and Pierre, J. L. *Tetrahedron* 32 (1976) 549.
- Rømning, C. and Sydnes, L. K. *Acta Chem. Scand. B* 31 (1977) 130.
- Kleveland, K. and Skattebøl, L. *Acta Chem. Scand. B* 29 (1975) 827.
- Srednev, S. S., Krynkov, S. I. and Farberov, M. I. *Zh. Org. Khim.* 10 (1974) 1608.
- Brouwer, H. and Stothers, J. B. *Can. J. Chem.* 50 (1972) 1361.
- Rozhkov, I. N. and Mabin, S. M. *Zh. Obshch. Khim.* 34 (1964) 59.
- Pansevitch-Kolyada, V. I. and Osipenko, J. F. *Zh. Obshch. Khim.* 28 (1958) 641.
- Ledwith, A. and Bell, R. M. *Chem. Ind. London* (1959) 459; Skattebøl, L. *J. Org. Chem.* 29 (1964) 2951.

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