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Chemistry of *gem*-Dihalocyclopropanes. XVII. Cyclopropylidene Insertion. Formation and Ring Opening of Bicyclo[1.1.0]butan-2-olate

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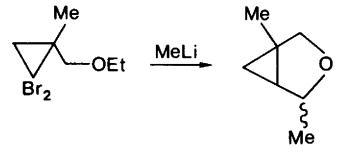
Reactions of *gem*-dibromocyclopropanemethanol derivatives *3a–3e* with methyllithium lead to allenic alcohols *4a–4h* and products which derive from ring opening of an intermediate bicyclo[1.1.0]-butan-2-olate (*17*). The latter is formed by insertion of the respective cyclopropylidene into a C–H bond. Evidence for *17* was obtained from deuterium labelling experiments. The ring opening generally occurs by a carbanion mechanism, but in the case of *3d* the intermediate bicyclobutanolate rearranged to the acyclic aldehyde *10*, apparently by a thermal mechanism. The secondary alcohols *3f–3h* reacted with methyllithium to give the corresponding allenes exclusively, which was also the case with ethers *3i–3l* derived from the primary alcohols.

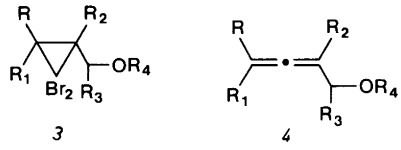
Insertion into σ-bonds and particularly C–H bonds is probably the most characteristic reaction of carbenes.[1] The carbene-like intermediate formed in reactions of *gem*-dihalocyclopropanes and alkyllithium has been shown to undergo both inter- and intramolecular insertion reactions into C–H bonds. In monocyclic systems intramolecular insertion occurs preferentially at carbon atoms three and five relative to the carbenyl carbon, leading to bicyclo[1.1.0]butanes and bicyclo[3.1.0]hexanes, respectively.

Baird[2] has shown that ethers like *1* undergo intramolecular insertion at a C–H bond adjacent to oxygen with formation of the bicyclic ether *2*; bicyclobutanes were not formed in any of these reactions. On the assumption that insertion into C–H bonds adjacent to oxygen is preferred, ethers and alcohols with such bonds available only at position three should yield bicyclobutanes. In a preliminary report[3] we have shown that *gem*-dibromocyclopropanemethanol derivatives react with methyllithium to form the respective bicyclo-[1.1.0]butanolate as intermediate. Such reactions have been previously reported to give only allenyl alcohols.[4] On the other hand, the corresponding *t*-butyl and trimethylsilyl ethers gave allenes as sole products. A full account of this study is reported here.

The *gem*-dibromocyclopropyl alcohols *3a–3h*



1 *2*



3 *4*

a: R=R$_1$=R$_2$=R$_3$=R$_4$=H
b: R=R$_1$=R$_3$=R$_4$=H; R$_2$=Me
c: R$_1$=R$_3$=R$_4$=H; R=R$_2$=Me
d: R$_3$=R$_4$=H; R=R$_1$=R$_2$=Me
e: R=R$_1$=R$_3$=R$_4$=H; R$_2$=Ph
f: R=R$_1$=R$_4$=H; R$_2$=R$_3$=Me
g: R$_1$=R$_4$=H; R=R$_2$=R$_3$=Me
h: R$_2$=R$_4$=H; R=R$_1$=R$_3$=Me
i: R=R$_1$=R$_3$=H; R$_2$=Me; R$_4$=*t*-Bu
j: R=R$_1$=R$_3$=H; R$_2$=Me; R$_4$=SiMe$_3$
k: R$_1$=R$_3$=H; R=R$_2$=Me; R$_4$=SiMe$_3$
l: R=R$_1$=R$_3$=H; R$_2$=Ph; R$_4$=SiMe$_3$

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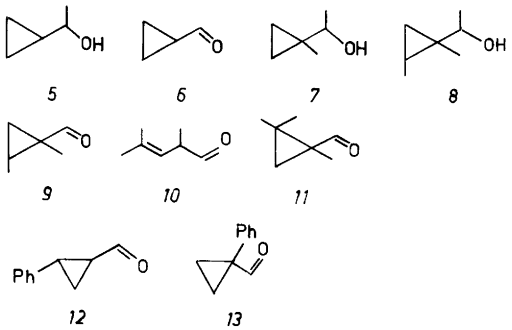
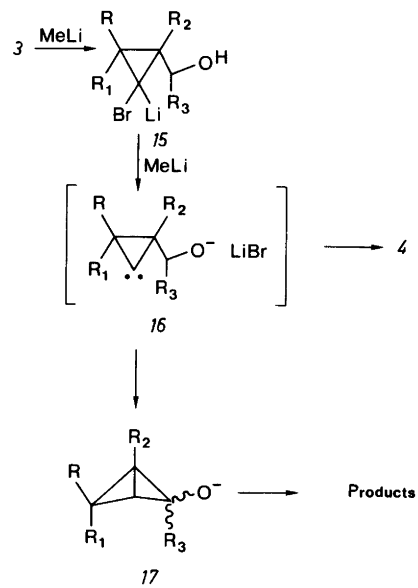
were prepared by addition of dibromocarbene to the respective allyl alcohol according to literature procedures. The ethers *3i* and *3j* were prepared from the respective β-methallyl ethers and dibromocarbene, and the remaining ethers, *3k* and *3l*, were prepared from the corresponding alcohols and chlorotrimethylsilane. Reactions of the alcohols *3a*–*3h* with methyllithium were in most cases carried out at −78 °C using more than two molar equivalents of methyllithium; reactions of the ethers were conveniently carried out at somewhat higher temperatures (−30 to 0 °C) and slightly more than one molar equivalent of the organolithium derivative was used. The reaction mixtures were analyzed by gas liquid chromatography (GLC) prior to work-up. The components of each product mixture were, as far as possible, separated by preparative GLC and identified spectroscopically. From some reactions the isolated yields were low due to extensive polymerization during distillation. Some of the results are recorded in Table 1.

With the exception of *3d*, the alcohols reacted to give some of the corresponding allenes *4*, and from the secondary alcohols *3f*–*3h* they were the sole products isolated in 80–90 % yields. The primary alcohols *3a*–*3c* gave derivatives of cyclopropanemethanol and cyclopropanecarbaldehyde as well. The reaction of the tetraalkylsubstituted dibromocyclopropane *3d* was unique in that the unsaturated aldehyde 2,4-dimethyl-3-pentenal (*10*)[5] was the main product. The alcohol *3e* also afforded aldehydes as major products. The compounds were characterized spectroscopically, in most cases by comparison with those of authentic samples. The aldehyde proton of *9* appeared at δ 8.61 in agreement with the published data for the *trans* isomer,[6] and the carbinol *8*[7] was shown to have the same configuration. The ^{1}H NMR spectrum of the aldehyde *12* is in agreement with that of the *trans* isomer.[8]



The ethers *3i*—*3l* reacted with methyllithium to give the corresponding allenes *4i*–*l* as sole products; however, in the case of *3l* it was necessary to carry out the reaction at 0 °C in order to avoid formation of the monobromide, 2-bromo-1-phenyl-1-trimethylsiloxymethylcyclopropane (*14*), which at −78 °C was actually a major product. Compound *14* was formed as the stereoisomer with the bromine and phenyl group *cis* related. Bicyclobutane derivatives were not obtained from any of these reactions.

The first step in reactions of *gem*-dibromocyclopropanes with alkyllithium is an exchange of bromine with lithium. There is evidence indicating that the bromine exchange is faster than proton abstraction from the hydroxyl group[9] in *gem*-dibromocyclopropanecarbinols; hence, we assume that the α-bromocyclopropyllithium intermediate *15* is formed initially in the present reaction. Whether α-elimination of lithium bromide from *15* precedes or follows anion formation is not clear; consequently, we cannot tell if the subsequent intramolecular insertion takes place on the alcohol or the corresponding anion. Lithium oxygen coordination stabilizes *15*, which suggests that anion formation occurs prior to α-elimination, and the carbene-like intermediate has been for simplicity pictured as *16* (Scheme 1). The stabilization of intermediates like *15* by adjacent oxygen functions has been exten-



Scheme 1.

Table 1. Reactions of 2,2-dibromocyclopropylmethanol derivatives with methyllithium.

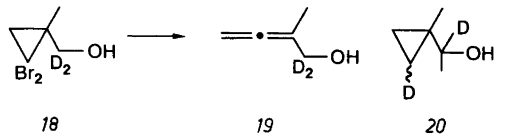
Starting material	Products (%)[a]		
3a	*4a*(56)	*5*(38)	*6*(6)
3b	*4b*(50)	*7*(50)	
3c	*4c*(75)	*8*(17)	*9*(8)
3d	*10*(91)	*11*(3)	
3e	*4e*(45)	*12*(35)	*13*(20)
3f	*4f*(100)		
3g	*4g*(100)		
3h	*4h*(100)		

[a] % of mixture determined by GLC; for yields see Experimental.

sively reported in the literature.[1,10]

Rearrangement to allenes was the expected reaction of the cyclopropylidenes *16*. The other products of Table 1 can all be explained by invoking the bicyclo[1.1.0]butanolate *17*, formed from *16* by intramolecular insertion into a C–H bond adjacent to oxygen. Cyclopropanol derivatives undergo base induced ring opening quite readily,[11] and it is not surprising that the highly strained intermediate *17* behaves similarly.

The cyclopropanecarbaldehydes produced may react further with methyllithium to the corresponding alcohols. The ring opening is apparently quite rapid since we failed in attempts to trap the bicyclobutanolate *17* as the corresponding ether by treating the reaction mixture from *3b* at −78 °C with either methyl iodide or chlorotrimethylsilane. The bicyclobutyl ether was expected to survive the reaction conditions; Hamon and Trenerry[12] have recently reported the isolation of the first example of this type of compound. Benzenethiol is known to react with bicyclobutanes by addition to the central bond,[13] but no phenylthiocyclobutanol derivative was obtained when the reaction mixture from *3b* was quenched at −78 °C with this reagent. However, labelling experiments provided conclusive evidence for the reaction path depicted in Scheme 1. We prepared the carbinol *18* labelled with deuterium at the α-carbon by reducing ethyl 2,2-dibromo-1-methylcyclopropanecarboxylate with lithium aluminium deuteride. Treatment of *18* with methyllithium afforded the expected allene *19* and the cyclopropylcarbinol *20* (Scheme 2). The allene was labelled at the methylene group as shown by the absence of the resonance at δ 3.92 in the ^{1}H NMR spectrum



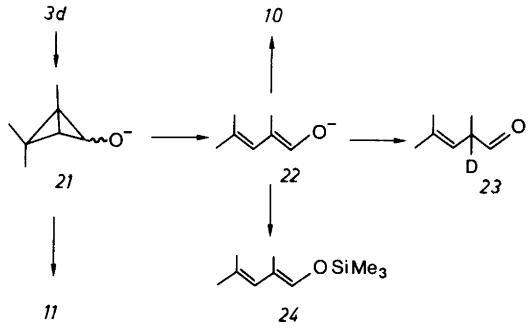
18 *19* *20*

Scheme 2.

and the collapse of the multiplet at δ 4.62 into a quartet. The most striking difference between the spectra of the alcohol *20* and its unlabelled analogue *7* is the complete absence in the former of the quartet at δ 3.08 due to the proton α to the hydroxyl group. With three chiral centres, *20* may be present as a mixture of diastereomers and the ^{1}H NMR spectrum clearly reveals that such a mixture of stereoisomers is indeed formed; the two methyl groups appear as five singlets while the cyclopropyl hydrogens exhibit a complex multiplet centred at δ 0.33. The cyclopropane derivatives formed are in accordance with ring opening of *17* to the most stable carbanion, and the formation of *trans*-2-phenylcyclopropanecarbaldehyde (*12*) indicates that protonation occurs with retention of configuration. Quenching of the reaction mixture from *3b* with D_2O caused no incorporation of deuterium in the ring, which suggests that the proton is abstracted from the solvent or from another proton donator in the reaction mixture.

The result from the reaction of compound *3d* is particularly interesting. It is not surprising that the allene was not encountered since tetraalkyl-substituted cyclopropylidenes seem to prefer insertion to ring opening,[14] and this reaction is no exception; at least 94 % of the product derives from the bicyclobutanolate *21*. Insertion occurs exclusively at the methylene C–H bonds adjacent to oxygen, but only a small amount of the product is formed by the carbanion mechanism while the major reaction path is apparently a thermal rearrangement of the bicyclobutanolate to the dienol anion *22*. Evidence for this mechanism was obtained from two experiments. First, quenching of the reaction mixture with D_2O gave the aldehyde *23* deuterated at the α carbon as shown by the absence of the multiplet centred at δ 3.15 in the parent compound. Secondly, treatment of the reaction mixture at −78 °C with chlorotrimethylsilane gave the dienol ether *24* (Scheme 3).

It is well established that bicyclo[1.1.0]butanes rearrange thermally to the corresponding 1,3-butadienes. The reaction may be a concerted [σ2s+



Scheme 3.

σ2a] process or proceed *via* diradicals, but for alkyl substituted derivatives temperatures of 200 °C or higher are required for the reaction to take place. Our reaction is rapid even at −78 °C and clearly the oxygen anion must exert a profound effect on the thermal stability of the bicyclobutane ring system. The observation is reminiscent of the dramatic rate-enhancing oxyanionic effect of the oxy-Cope rearrangement, first discovered by Evans;[15] unfortunately, in our case a fair comparison is not available since 2-bicyclo[1.1.0]butanol and derivatives are unknown.

According to Hammet $\sigma-\rho$ correlation there seems to be little build-up of charge at carbon in the transition state of cyclopropylidene insertion.[16] It has been reported that the preference for insertion into C−H bonds follow the order: *tert*>*sec*>*prim.*[17] Moreover, there are many examples in the literature which show a preference for both inter- and intramolecular insertion into C−H bonds adjacent to an ether oxygen;[1,2] however, in the case of 1,3-insertion with formation of bicyclobutyl ethers such a preference has not been observed. There are indications that a methoxy group actually retards the 1,3-insertion into the adjacent C−H bond.[18] On the assumption that substituents on C−3 do not significantly affect the rate of ring opening to allene, our results indicate that the oxide ion facilitate insertion while an ether function does not. It is also interesting that a secondary C−H bond is preferred; with tertiary C−H bonds (compounds *3f*−*3h*, Table 1) only allenes were formed. With the data available so far, it is not easy to see any trend in the C−H insertion reactions of cyclopropylidenes which can be simply correlated with electronic and steric effects.

EXPERIMENTAL

The NMR spectra were recorded on Varian EM 360A or Jeol JNM FX60 instruments. Tetramethylsilane was used as internal standard except for the trimethylsilyl ethers for which chloroform was used. Elemental analyses were performed by Ilse Beetz Microanalytical Laboratory, 8640 Kronach, West Germany.

trans-*2,2-Dibromo-1,3-dimethyl-1-(trimethylsiloxymethyl) cyclopropane (3k)* was prepared in 60 % yield from the alcohol *3c* and trimethylchlorosilane using dimethylanilin as base, b.p. 63−66 °C (0.1 mmHg); Anal. for $C_9H_{18}OSi$:C,H. ^{1}H NMR (CCl_4): δ 0.08 (9H,s) 1.07 (3H,d, J = 2.0 Hz) 1.1 (1H,m) 1.12 (3H,s) 3.42 (2H,s).

2,2-Dibromo-1-phenyl-1-(trimethylsiloxymethyl) cyclopropane (3l) was prepared in 52 % yield from the alcohol *3e* and trimethylchlorosilane using dimethylanilin as base, b.p. 76 °C (0.04 mmHg) n_D^{23} 1.5441; Anal. for $C_{13}H_{18}Br_2OSi$: C,H. ^{1}HNMR (CCl_4): δ −0.14 (9H,s) 1.90 (2H,m) 3.87 (2H,d), 7.21 (5H,s).

2,2-Dibromo-1-methyl-1-(trimethylsiloxymethyl) cyclopropane (3j) was prepared by the Doering-Hoffmann procedure[19] in 35 % yield from 2-methyl-1-trimethylsiloxy-2-propene,[20] bromoform and potassium *t*-butoxide, b.p. 65−68 °C (0.4 mmHg); Anal. for $C_8H_{16}Br_2OSi$; C,H. ^{1}HNMR (CCl_4): δ 0.12 (9H,s) 1.41 (3H,s) 1.45 (2H,m) 3.67 (2H,s).

*2,2-Dibromo-1-methyl-1-*t*-butoxymethylcyclopropane (3i)* was prepared in 54 % yield by the phase transfer procedure[21] from 2-methyl-1-*t*-butoxy-1-propene,[22] bromoform, 50 % aq. sodium hydroxide and triethylbenzylammonium chloride as catalyst, b.p. 54−55 °C (0.5 mmHg), n_D^{18} 1.4937; Anal. for $C_9H_{16}Br_2O$; C,H. ^{1}HNMR (CCl_4): δ 1.17 (9H,s) 1.40 (3H,s) 1.5 (2H,m) 3.38 (2H,s).

Reactions of 2,2-dibromocyclopropanemethanol derivatives with methyllithium. General procedure. A 1.5−1.7 M solution of methyllithium in ether (2 molar equivalents) was added dropwise to a stirred and cooled (−30 to −78 °C, bath temp.) solution of the dibromocyclopropane derivative (1.0 molar equivalent) in dry ether. The reaction mixture was stirred for 0.5−3 h at bath temperature after the addition was completed, allowed to warm and decomposed with water. The product was extracted with ether. The dried ($MgSO_4$) extract was evaporated to give the crude product which was purified by distillation and/or preparative gas chromatography.

Reaction of (2,2-Dibromocyclopropanemethanol (3a). A solution of *3a*[23] (3.5 g, 15.2 mmol) in 15 ml of dry ether was treated with 26.5 ml of 1.7 M methyllithium (45 mmol) at −78 °C. Distillation gave 0.45 g of product, b.p. 45−47 °C (18 mmHg)

consisting of 2,3-butadien-1-ol (*4a*; 56 %),[24] 1-cyclopropylethanol (*5*; 38 %)[25] and cyclopropanecarbaldehyde (*6*; 6 %).[6] The spectral data were identical with those reported in the literature. Extensive polymer formation took place during distillation.

Reaction of 2,2-Dibromo-1-methylcyclopropane methanol (3b). A solution of *3b*[26] (112.7 g), 0.46 mol) in 150 ml of dry ether was treated with 650 ml of 1.7 M methyllithium (1.1 mol) at −50 °C. Distillation gave 11.9 g of product, b.p. 54−57 °C (26 mmHg) consisting of 2-methyl-2,3-butadien-1-ol (*4b*; 50 %)[27] and 1-(1-methylcyclopropyl)ethanol (*7*; 50 %).[28] The spectral data were in accordance with those reported in the literature. Extensive polymer formation occurred during distillation of the product.

Reaction of 2,2-Dibromo-1,3-dimethylcyclopropane methanol (3c). A solution of *3c*[26] (6.2 g; 25 mmol) in 25 ml of dry ether was treated with 35 ml of 1.6 M methyllithium (56 mmol) at −30 °C. The crude product (2.8 g) consisted of 2-methyl-2,3-pentadien-1-ol (*4c*; 75%), 1-(*cis*-1,2-dimethylcyclopropane) ethanol (*8*: 17 %)[7] and *trans*-1,2-dimethylcyclopropanecarbaldehyde (*9*; 8 %).[6] These were separated by prep. GLC and the spectral data of *8* and *9* were in accordance with those in the literature. (*4c*): IR (film) 1960 cm^{-1}. ^1H NMR (CCl_4): 1.64 (3H,d, J = 4.0 Hz) 1.72 (3H,s) 2.5 (1H, broad s) 3.90 (2H,d, J = 2.5 Hz) 5.15 (1H,m).

Reaction of 2,2-Dibromo-1,3,3-trimethylcyclopropane methanol (3d). A solution of *3d*[29] (1.9 g, 7.0 mmol) in 10 ml of dry ether was treated with 9.6 ml of 1.5 M methyllithium (14.4 mmol) at −78 °C. The crude product (1.0 g) consisted of 2,4-dimethyl-3-pentenal (*10*; 91 %),[5] 1,2,2-trimethylcyclopropanecarbaldehyde (*11*; 3 %) and two other unidentified components (2 and 4 %). The spectral data of *10* were identical with those in the literature. *11*: ^1H NMR (98 MHz; CCl_4): δ 0.7 (2H,m) 1.29 (3H,s) 1.34 (3H,s) 1.36 (3H,s) 9.30 (1H,s). Hydrolysis of the above reaction mixture with D_2O gave 2-deutero-2,4-dimethyl-3-pentenal (*23*): ^1H NMR (98 MHz; CCl_4): δ 1.3 (3H,s) 1.81 (3H,s), 1.87 (3H,s) 5.02 (1H, broad s) 9.48 (1H,s).

Reaction of 2,2-Dibromo-1-phenylcyclopropane methanol (3e). A solution of *3e*[30] (6.04 g; 20 mmol) in 20 ml of dry ether was treated with 26.0 ml of 1.8 M methyllithium (45 mmol) at −78 °C to give 2.0 g of a liquid, b.p. 78 °C (0.05 mmHg) consisting of 2-phenyl-2,3-butadien-1-ol (*4e*; 45%),[27] *trans*-2-phenylcyclopropanecarbaldehyde (*12*; 35 %)[8] and 1-phenyl-cyclopropanecarbaldehyde (*13*; 20 %).[31] All the compounds exhibited spectral data in accordance with those reported in the literature.

3-Methyl-3,4-pentadien-3-ol (*4f*)[4] was obtained in 83 % yield from 1-(2,2-dibromo-1-methylcyclopropane) ethanol (*3f*)[4] and methyllithium at −55 °C.

3-Methyl-3,4-hexadien-2-ol (*4g*) was obtained in 90 % yield, b.p. 57−58 °C (13 mmHg) n_D^{22} 1.4760, from *trans*-1-(2,2-dibromo-1,3-dimethylcyclopropane)ethanol (*3g*)[27] and methyllithium at −78 °C.

5-Methyl-3,4-hexadien-2-ol (*4h*)[4] was obtained in 90 % yield from 1-(2,2-dibromo-3,3-dimethylcyclopropane)ethanol (*3h*)[4] and methyllithium at −78 °C.

2,4-Dimethyl-1-(trimethylsiloxy)-1,3-pentadiene (*24*). To the reaction mixture from *3d* (0.20 g; 0.74 mmol) and methyllithium (1.65 mmol) kept at −78 °C was added trimethylchlorosilane (0.33 g; 3.0 mmol. After stirring at this temperature for 15 h, the reaction mixture was allowed to attain room temperature. Usual work-up resulted in 0.2 g crude product consisting essentially of *24*: ^{1}HMNR (CCl_4): δ 0.17 (9H,s) 1.25 (3H,s) 1.60 (3H,s) 1.68 (3H,s) 5.37 (1H,s) 5.97 (1H,s). ^{13}C NMR (CCl_4): δ 3.50 (Si−CH_3), 15.84, 21.43, 28.89 (CH_3) 118.50 (olef. C) 127.07 (olef. CH) 131.81 (olef. C) 139.53 (=CH−O−).

2-Methyl-1-t-butoxy-2,3-butadiene (4i). A solution of *3i* (1.5 g; 5.0 mmol) in 5 ml of dry ether was treated with 3.3 ml of 1.7 M methyllithium (5.5 mmol) to give 0.7 g (100 %) of crude *4i*, which was purified by prep. GLC; IR (film): 1955, 880, 845 cm^{-1}. ^{1}HNMR (CCl_4): δ 1.07 (9H,s) 1.67 (3H,t, J = 3.0 Hz) 3.78 (2H,t, J = 2.0 Hz) 4.55 (2H,m).

2-Methyl-1-trimethylsiloxy-2,3-butadiene (4j). A solution of *3j* (3.1 g; 10.0 mmol) in 15 ml of dry ether was treated with 8.8 ml 1.8 M methyllithium (15.0 mmol) at −78 °C to give 1.6 g (100 %) of crude *4j*, which was purified by prep. GLC; IR (film): 1960, 860 cm^{-1}. ^{1}HNMR (CCl_4): δ −0.03 (9H,s) 1.57 (3H,t, J = 3.0 Hz) 3.93 (2H,t, J = 2.0 Hz) 4.48 (2H,m).

2-Methyl-1-trimethylsiloxy-2,3-pentadiene (4k). A solution of *3k* (1.25 g; 3.8 mmol) in 5 ml of ether was treated with 2.5 ml of 1.6 M methyllithium (4.0 mmol) at −30 °C to give 0.46 g (71 %) of *4k*; IR (film) 1960 cm^{-1}; ^{1}HNMR (CCl_4) δ 0.15 (9H, s) 1.62 (3H,d, J = 5.5 Hz) 1.70 (3H,s) 4.06 (2H,d, J = 2.0 Hz) 5.1 (1H, broad m).

2-Phenyl-1-trimethylsiloxy-2,3-butadiene (4l). A solution of *3l* (4.0 g; 11 mmol) in 10 ml of dry ether was treated with 8.0 ml of 1.7 M methyllithium (13.6 mmol) at −78 °C to give a mixture of 2-phenyl-1-trimethylsiloxy-2,3-butadiene (*4l*; 50 %) and 2-bromo-1-phenyl-1-trimethylsiloxymethylcyclopropane (*14*; 50%). The allene decomposed on attempted distillation. *4l*: IR (film): 1960 cm^{-1}. ^1H NMR (CCl_4): δ 0.10 (9H,s) 3.70 (2H,t, J = 2Hz), 4.70 (2H,m). *14*: b.p. 70−75 °C (0.13 mmHg); ^1H NMR (CCl_4): δ 0.07 (9H,s) 1.42 (2H,m) 3.16 (1H,m) 3.66 (2H,s) 7.23 (5H,s).

2,2-Dibromo-1-methylcyclopropane α,α-*dideutero-*

methanol (*18*) was prepared in 86 % yield from ethyl 2,2-dibromo-1-ethylcyclopropanecarboxylate[32] by selective reduction using lithium aluminium deuteride as described for the hydrogen analog;[30] recrystallization from pentane gave the pure compound, m.p. 70 °C; ^{1}H NMR ($CDCl_3$): δ 1.52 (3H,s), 1.55 (2H, ABq, J = 7.5 Hz), 1.94 (1H,s).

Reaction of 2,2-Dibromo-1-methylcyclopropane α,α-dideuteromethanol (*18*). The reaction was carried out as described for *3b*. The product was shown to consist of 1,1-dideutero-2-methyl-2,3-butadien-1-ol (*19*; 59 %) and 1-deutero-1-(2-deutero-1-methylcyclopropane)ethanol (*20*; 41 %). *19*: IR (film) 2090, 1960, 850 cm^{-1}. ^{1}H NMR (CCl_4): δ 1.70 (3H,t, J = 3.5 Hz) 3.43 (1H,s) 4.66 (2H,q, J = 3.5 Hz). *20*: ^{1}H NMR (CCl_4): δ 0.33 (3H,m) 1.2 (6H,m) 3.5 (1H, broad s).

REFERENCES

1. Kirmse, W. *Carbene Chemistry*, 2nd Ed., Academic, New York 1971; Jones, W. M. and Brinker, U. H. In Marchand, A. P. and Lehr, R. E., Eds., *Pericyclic Reactions*, Academic, New York 1977, Vol. 1.
2. Baird, M. S. *Chem. Commun.* (1971) 1145.
3. Nilsen, N. O., Sydnes, L. K. and Skattebøl, L. *Chem. Commun* (1978) 128.
4. Maurin, R. and Bertrand, M. *Bull. Soc. Chim. Fr.* (1972) 2349.
5. Matteson, D. S., Moody, R. J. and Jesthi, P. K. *J. Am. Chem.* Soc. *97* (1975) 5608.
6. Ripoll, J.-L. and Conia, J.-M. *Bull. Soc. Chim. Fr.* (1965) 2755.
7. Manning, P. C., Jr. *J. Org. Chem. 44* (1979) 2461.
8. Scribe, P. and Wiemann, J. *Bull. Soc. Chim. Fr.* (1971) 2268.
9. Seebach, D., Siegel, H., Gabriel, J. and Hässig, R. *Helv. Chim. Acta 63* (1980) 2046 and references therein.
10. Taylor, K. G., Hobbs, W. E. and Saquet, M. *J. Org. Chem. 36* (1971) 369.
11. Gibson, D. H. and De Puy, C. H. *Chem. Rev. 74* (1974) 605.
12. Hamon, D. P. G. and Trenerry, V. C. *Aust. J. Chem. 33* (1980) 809.
13. Szeimies, G., Schlosser, A., Philipp, F., Dietz, P. and Mickler, W. *Chem. Ber. 111* (1978) 1922.
14. Skattebøl, L. *Tetrahedron Lett.* (1970) 2360; Moore, W. R., Taylor, K. G., Müller, P., Hall, S. S. and Gaibel, Z. L. F. *Ibid.* (1970) 2365; Moore, W. R. and Hill, J. B., *Ibid.* (1970) 4343, 4553; Reinharz, R. B. and Fonken, G. J. *Ibid.* (1974) 441; Hamon, D. P. G. and Trenerry, V. C. *Ibid.* (1974) 1371; Shono, T., Nishiguchi, I., Komamura, T. and Fujita, K. *Ibid.* (1977) 4327; Hamon, D. P. G. and Trenerry, V. C. *Aust. J. Chem. 33* (1980) 809.
15. Evans, D. A. and Bolob, A. M. *J. Am. Chem. Soc. 97* (1975) 4765; Crouse, G. D. and Paquette, L. A. *Tetrahedron Lett.* (1981) 3167 and references therein.
16. Baird, M. S. *Chem. Commun.* (1979) 776.
17. Moore, W. R. and Hill, J. B. *Tetrahedron Lett.* (1970) 4343; Moore, W. R. and King, B. I. *J. Org. Chem. 36* (1971) 1877; Paquette, L. A., Wilson, S. E., Henzel, R. P. and Allen, G. E. *J. Am. Chem. Soc. 94* (1972) 7761; Reinarz, R. B. and Fonken, G. J. *Tetrahedron Lett.* (1973) 4013.
18. Paquette, L. A. and Taylor, R. T. *J. Org. Chem. 39* (1974) 2677.
19. Doering, W. von E. and Hoffmann, A. K. *J. Am. Chem. Soc. 76* (1954) 6162; Skattebøl, L. and Solomon, S. *Org. Synth. 49* (1969) 35.
20. Kozlikov, V. L., Fedotov, N. S. and Mironov, V. F. *Zh. Obshch. Khim. 39* (1969) 2284.
21. Dehmlow, E. V. and Dehmlow, S. S. *Phase Transfer Catalysis*, Verlag Chem., Weinheim, Deerfield Beach, Basel 1980.
22. Olson, W. T., Hipsher, H. F., Buess, C. M., Goodman, I. A., Hart, Z., Lamneck, J. H. and Gibbons, L. C. *J. Am. Chem. Soc. 69* (1947) 2451.
23. Holm, K. H., Lee, D. G. and Skattebøl, L. *Acta Chem. Scand. B 32* (1978) 639.
24. Karlsen, S., Frøyen, P. and Skattebøl, L. *Acta Chem. Scand. B 30* (1976) 665.
25. Pierre, J.-L., Perraud, R. and Arnaud, P. *Bull. Soc. Chim. Fr.* (1969) 1322.
26. Kleveland, K., Skattebøl, L. and Sydnes, L. K. *Acta Chem. Scand. B 31* (1977) 463.
27. Gelin, R., Gelin, S. and Albrand, M. *Bull. Soc. Chim. Fr.* (1971) 4146.
28. Julia, M., Noël, Y. and Guégan, R. *Bull. Soc. Chim. Fr.* (1968) 3742.
29. Sydnes, L. K. *Acta Chem. Scand. B 32* (1978) 47.
30. Sydnes, L. K. and Skattebøl, L. *Acta Chem. Scand. B 32* (1978) 632.
31. Küntzel, H., Wolf, H. and Schaffner, K. *Helv. Chim. Acta 54* (1971) 868.
32. Sydnes, L. K., Skattebøl, L., Chapleo, C. B., Leppard, D. G., Svanholt, K. L. and Dreiding, A. S. *Helv. Chim. Acta 58* (1975) 2061.

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