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Chemistry of *gem*-Dihalocyclopropanes. XIV. Reactions of *gem*-Dibromocyclopropyl Ketones and Alkyl *gem*-Dibromocyclopropanecarboxylates with Methyllithium

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Treatment of mono- and disubstituted *gem*-dibromocyclopropyl ketones and esters with methyllithium resulted in the formation of complex reaction mixtures, but in most cases the main volatile product was the corresponding monobromocyclopropyl derivative. Reactions of 2-acetyl-1,1-dibromo-2,3,3-trimethylcyclopropane and 1,1-dibromo-2-isobutyryl-2,3,3-trimethylcyclopropane with methyllithium gave mixtures of isomeric bicyclo-[1.1.0]butanes; in the latter case 1,3,3,5,5-pentamethylbicyclo[2.1.0]pentan-2-one was formed as a by-product.

gem-Dibromocyclopropanes substituted with alkoxy,[1–8] amino,[9,10] and hydroxyl [11–13] groups, respectively, have been treated with methyllithium; however, similar reactions with derivatives containing an acyl or an alkoxycarbonyl group had not been reported when the present work was initiated. A preliminary account of our studies has been published,[14] and Barlet has recently reported some results on such reactions.[15]

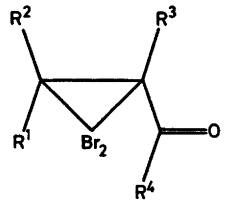


Fig. 1. $R^1=R^2=H$; $R^3=R^4=CH_3$ (*1*); $R^1=H$, $R^2=R^3=R^4=CH_3$ (*6*); $R^1=R^2=R^3=CH_3$, $R^4=CH(CH_3)_2$ (*9*); $R^1=R^2=R^3=R^4=CH_3$ (*16*); $R^1=R^2=H$, $R^3=CH_3$, $R^4=OCH_3$ (*19*).

RESULTS

The compounds studied (Fig. 1) were prepared by the addition of dibromocarbene to α,β-unsaturated ketones and esters.[16] The reactions of the *gem*-dibromocyclopropyl ketones and esters with an excess of methyllithium (molar ratio usually 1:1.1) were carried out in the temperature range of −115 to 10 °C by normal addition of base to the substrate or by inverse addition. GLC analysis was always performed on the crude reaction mixture prior to evaporation of the solvent and, when feasible, pure samples of each product were obtained by preparative GLC. In most cases the main volatile product turned out to be the corresponding monobromocyclopropyl ketone or ester, while allenes were not detected in any of the experiments.[17]

The reaction of 2-acetyl-1,1-dibromo-2-methylcyclopropane (*1*) gave at −78 °C a single volatile product which was shown by NMR to be (*E*)-2-acetyl-1-bromo-2-methylcyclopropane (*2E*).[18] The yield of *2E* was 5 % when the base was added to *1* and 43 % when the reaction was performed with inverse addition. In either case, the main product was a yellow, viscous residue which exhibited IR absorptions characteristic of hydroxyl groups, carbonyl groups, and C−Br bonds. (*E*)-1-Acetyl-1,2-dimethylcyclopropane which according to Barlet is the main product from this reaction at temperatures below −30 °C,[15] was not observed.

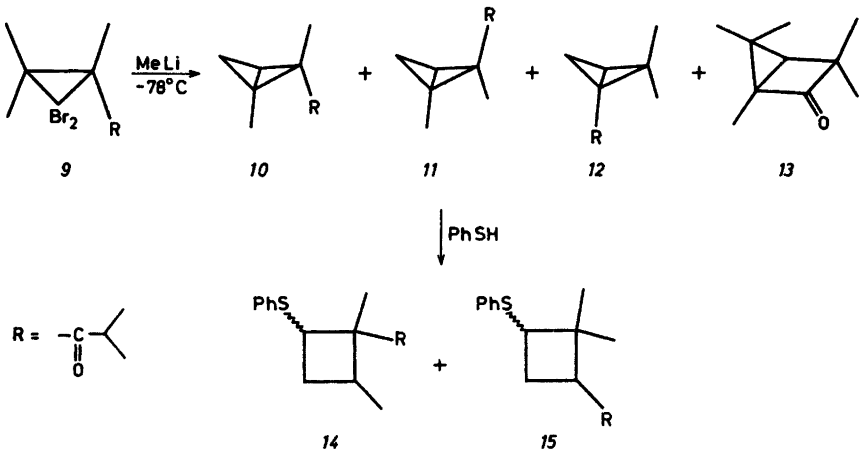
When *1* was allowed to react at −115 °C with methyllithium added in the normal way, distillation of the crude product afforded some

water and a mixture of six compounds in a total yield of 25 %. Four of these, which represented 80 % of the mixture, were separated by preparative GLC and characterized as *2E*, *2Z*, (*Z*)-1-bromo-2-isopropenyl-2-methylcyclopropane (*3*),[19,20] and (*Z*)-2-acetyl-1-bromo-1,2-dimethylcyclopropane (*4*). The stereochemistry of the last compound was assigned on the basis of the ^{1}H NMR spectrum. The signal at δ 1.45 due to the 2-methyl group appears at a field requiring an *E* relationship to the bromine atom; the same methyl group in the related isomers *2E* and *2Z* appears as a singlet at δ 1.57 and 1.44, respectively.[18,19] Compound *3* cannot be a product of the reaction, but is formed during distillation from the alcohol 2-[(*Z*)-2-bromo-1-methylcyclopropyl]-propan-2-ol (*5Z*); this accounts for the water produced during work-up. Alcohol *5Z* most probably resulted from reaction of *2Z* with methyllithium and an authentic sample of the former compound was prepared in this way.

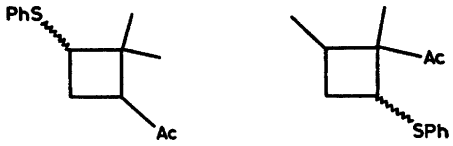
Normal addition of methyllithium to (*E*)-2-acetyl-1,1-dibromo-2,3-dimethylcyclopropane (*6*) kept at −78 °C gave a reaction mixture consisting of two compounds in a ratio of 3:2. The major product, isolated in 50 % yield, was shown to be (2*E*,3*Z*)-2-acetyl-1-bromo-2,3-dimethylcyclopropane (*7*) whereas the minor product, isolated in 20 % yield, was 2-[(3*E*)-2-bromo-1,3-dimethylcyclopropyl]-propan-2-ol (*8*). The ^{1}H NMR spectrum of the latter compound exhibits a doublet with *J* 7 Hz for the hydrogen atom geminal to the bromine atom which therefore must be situated *E* to the hydroxyl function.

The reaction of 1,1-dibromo-2-isobutyryl-2,3,3-trimethylcyclopropane (*9*) with methyllithium took a quite different course as no products containing either hydroxyl groups or bromine atoms were formed. According to GLC/MS analysis at least three products with composition $C_{10}H_{16}O$, isolated in 90 % yield, were formed. All attempts to separate these isomers were unsuccessful and the products were therefore analyzed spectroscopically as a mixture. The ^{1}H NMR spectrum shows absorptions attributable to the bicyclo[1.1.0]-butanes *10* – *12* (Scheme 1), but in addition signals due to a minor product are present. Of particular interest in the IR spectrum is a band at 1815 cm^{-1} which is indicative of a strained cyclobutanone.[21] The minor product is therefore most likely 1,3,3,5,5-pentamethylbicyclo[2.1.0]pentan-2-one (*13*) and the additional peaks in the ^{1}H NMR spectrum are not in disagreement with this assignment; furthermore, the bicyclobutanes *10* – *12* and bicyclopentanone *13* are formed in an approximate ratio of 9:1.

Further support for the results summarized in Scheme 1 was obtained by treatment of the mixture of ketones *10* – *13* with benzenethiol.[22] According to spectroscopic evidence, high-resolution MS, and elemental analysis a complex mixture of isobutyryldimethylphenylthiocyclobutanes *14* and *15* was obtained in 90 % yield (Scheme 1). GLC analysis revealed the presence



Scheme 1.



17 18

Fig. 2. Compounds *17* and *18*.

of five isomers which were not separated. The bicyclopentanone *13* reacted also with thiophenol, but products due to this reaction were not isolated.

Similar treatment of 2-acetyl-1,1-dibromo-2,3,3-trimethylcyclopropane (*16*) with methyllithium followed by reaction with benzenethiol resulted in the formation of an isomeric mixture of the phenylthiocyclobutanes *17* and *18* (Fig. 2) in 50 % overall yield.

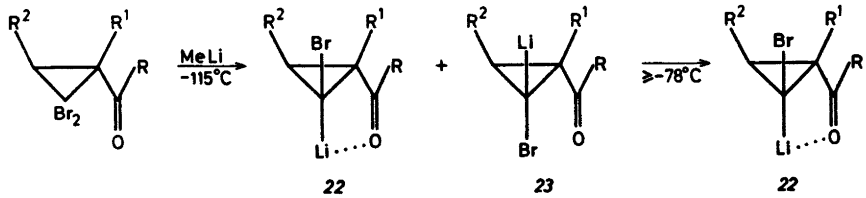
From reactions of methyl 2,2-dibromo-1-methylcyclopropanecarboxylate (*19*) with methyllithium under a variety of conditions the temperature turned out to be the main factor affecting the composition of the reaction mixture. At −78 °C a mixture of four volatile products was isolated in moderate yield. About 80 % of this mixture comprised of *2E*, but the structures of the three other components remain uncertain. At −115 °C, however, a complex mixture of nine compounds was obtained. Distillation afforded a mixture of the three major products which were separated by preparative GLC and identified on the basis of spectroscopic data as methyl (*E*)-2-bromo-1-methylcyclopropanecarboxylate (*20E*), *20Z*, and methyl (*Z*)-2-bromo-1,2-dimethylcyclopropanecarboxylate (*21*). The configuration of *18* was assigned on the basis of similar arguments as those presented for compound *4*; the position in the ^{1}H NMR spectrum of the 1-methyl group (δ 1.37) is best accommodated by the *Z* configuration. Similar results were obtained when ethyl 2,2-dibromo-1-methyl-cyclopropanecarboxylate reacted with methyllithium under variable conditions.

DISCUSSION

It is well-known that reactions of *gem*-dibromocyclopropanes with methyllithium occur with an initial lithium-bromine exchange leading to the corresponding bromolithio derivatives.[23] This process is strongly influenced by substituents attached to the ring, and replacement of an alkyl or hydroxyalkyl group with a carboxylic function results in a large rate enhancement.[15,18] It is therefore not surprising that in the above reactions methyllithium undergoes metal-halogen exchange considerably faster than addition to carbonyl groups.

Methyllithium can react with either of the bromine atoms [24] resulting in the formation of two isomeric organolithium derivatives which are interconvertible due to the epimerization of 1-bromocyclopropyl anions.[25] Usually such intermediates are unstable and eliminate lithium bromide with the formation of a carbene or carbenoid. However, stabilization of one of the isomeric organolithium derivatives has been observed in cases where the oxygen atom of an ether function can coordinate intramolecularly with lithium;[1,2,4–7] the products formed will then derive from this isomer.

Similarly the existence of intramolecular stabilization of *gem*-bromolithiocyclopropyl ketones and esters by coordination with the carbonyl group explains the formation of most of the products identified from reactions of the mono- and disubstituted derivatives with methyllithium. As outlined in Scheme 2 we suggest that at −115 °C equilibrium of the stereoisomeric organolithium derivatives *22* and *23* is slow and mixtures of stereoisomers are formed; however, at −78 °C and above the



22 23 22

Scheme 2.

only isomer present is *22* which is stabilized by coordination and stereospecific reactions result. In addition the high-boiling residues formed probably result from intermolecular condensation of organolithium intermediates as well as their reactions with unreacted starting material;[26] consequently, inverse addition of the base should reduce the amount of such products which turned out to be the case. Furthermore, the monobromides *4* and *21* are formed by displacement on methyl bromide [27–29] which results from the lithium-bromine exchange reaction.

On the other hand, the reactions of the trisubstituted *gem*-dibromocyclopropyl ketones *9* and *16* with methyllithium must involve carbenes or carbenoids which undergo intramolecular insertion into C–H bonds yielding mixtures of bicyclic products.[22,30] For reasons that are not quite clear tetrasubstituted *gem*-dihalocyclopropanes are particularly prone to undergo such reactions, but examples of less substituted derivatives undergoing this reaction are also known.[3,10,13,31] It is interesting that the cyclopropylidene derived from ketone *9* inserts predominantly into primary C–H bonds, in agreement with some [32,33] but contrary to other [34–36] results reported previously for a number of cyclopropylidene insertion reactions; the selectivity rule *tert* > sec > prim for these reactions must therefore be treated with care. Obviously, both steric and electronic effects seem to play an important part in determining the selectivity of carbene insertion reactions.

EXPERIMENTAL

General. Most of the apparatus employed have been described elsewhere.[37] The GLC/MS analyses were performed on a Perkin Elmer 990 gas chromatograph coupled with a Hitachi-Perkin Elmer RMU–GL mass spectrometer. Elemental analyses were carried out by Ilse Beetz Microanalytical Laboratory, 8640 Kronach, West Germany.

Starting materials. The ketones and esters employed were prepared as described in the literature.[16]

Treatment of gem*-dibromocyclopropane derivatives with methyllithium.* The reactions were carried out under pure nitrogen.

Method A (Normal addition). An ethereal solution (1.0–1.75 M) of methyllithium (20–44 mmol) was added dropwise to a cooled (10 to −115 °C), stirred solution of a *gem*-dibromocyclopropane derivative (20 mmol) in dry ether (30–50 ml). The reaction mixture was stirred for another 1–2 h at bath temperature. Then it was hydrolyzed with water (20 ml) and extracted with ether; the combined organic fractions were dried ($MgSO_4$). Evaporation of the ether left a residue which was purified by distillation.

Method B (inverse addition). An ethereal solution (1.75 M) of methyllithium, 25 ml (44 mmol), was diluted with dry ether (usually 20–40 ml) and stirred at −35 to −78 °C. During 5–15 min 20 mmol of a *gem*-dibromocyclopropane derivative in 20–40 ml of dry ether was added dropwise. The reaction mixture was stirred for 1–2 h at bath temperature and then worked up as described above.

The following substrates were allowed to react with methyllithium according to either or both of the methods.

2-Acetyl-1,1-dibromo-2-methylcyclopropane (*1*) was treated with methyllithium at −78 and −115 °C.

−78 °C: (*E*)-2-Acetyl-1-bromo-2-methylcyclopropane (*2E*) [18] was isolated in a yield of 5 % and 43 % when the reaction was performed according to method A and method B, respectively, b.p. 61–62 °C/8.5 mmHg (lit.[19] b.p. 32 °C/0.06 mmHg). The IR spectra of the residues showed bands at 3600 (s), 1700 (w) and 690 (w) cm^{-1}.

−115 °C: When 10.2 g (40 mmol) of *1* reacted with 44 mmol of methyllithium according to method A, 1.5 g of volatile products were isolated in addition to some water. GLC analysis (20 % SE30, 115 °C) revealed six compounds which were separated by preparative GLC (same conditions). Based on spectroscopic data the structures of four were assigned as listed below in order of increasing retention time (relative yield in parantheses): (*Z*)-1-Bromo-2-isopropenyl-2-methylcyclopropane (*3*) [19,20] (15 %). (*Z*)-2-Acetyl-1-bromo-2-methylcyclopropane (*2Z*) [19] (45 %). (*Z*)-2-Acetyl-1-bromo-1,2-dimethylcyclopropane (*4*) (24 %); the compound was not obtained pure enough for elemental analysis. ^1H NMR (98 MHz CCl_4): δ 0.72 (1 H d, *J* 6.5 Hz), 1.45 (3 H, s), 1.90 (3 H, s), 1.94 (1 H, d, *J* 6.5 Hz), 2.25 (3 H, s). IR (CCl_4): 1715 (s), 1370 (m), 1200 (w), 1130 (m), 1040 (w), 870 (w) cm^{-1}. *1* (16 %).

In addition small amounts of impure *2E* were isolated.

(E)-2-Acetyl-1,1-dibromo-2,3-dimethylcyclopropane (6) was allowed to react with methyllithium at −78 °C according to method A. GLC (20 % SE30, 120 °C) revealed the presence of two products in a ratio of 3:2, (*2E,3Z*)-2-acetyl-1-bromo-2,3-dimethyl-cyclopropane (*7*), b.p. 38 °C/0.20 mmHg (lit.[19] 44 °C/0.85 mmHg for an isomeric mixture), and 2-[(3*E*)-2-bromo-1,3-dimethylcyclopropyl]propan-2-ol (*8*), b.p. 48 °C/0.25 mmHg. The latter compound was

not obtained pure enough for elemental analysis. ^{1}H NMR (60 MHz, CCl_4): δ 1.06 (3 H, s), 1.18 (6 H, s), 1.27 (3 H, d, J 6 Hz), 1.30–1.80 (1 H, m), 1.97 (1 H, s), 3.41 (1 H, d, J 7 Hz). IR (film): 3390 (m), 1115 (m), 1080 (w), 690 (w) cm^{-1}.

1,1-Dibromo-2-isobutyryl-2,3,3-trimethylcyclopropane (9) was treated with methyllithium at −78 °C according to method A. A mixture of low-boiling products was formed, b.p. 30–36 °C/0.75 mmHg. The mixture was proved to consist of isomers with composition $C_{10}H_{16}O$ by GLC/MS (2 % Dexsil 300, 70 °C/70 eV). The isomers were not separated pure. IR (film) of the mixture: 1815 (s), 1685 (s), 1385 (m), 1365 (m), 1210 (m), 1005 (w), 965 (w), 955 (w) cm^{-1}. The ^{1}H NMR spectrum of the mixture is described as if the isomers were observed separately. ^{1}H NMR (bicyclo[1.1.0]butane derivatives *10–12*) (60 MHz, CCl_4): δ 1.05–1.62 (3 H, m), 1.12 and 1.14 (6 H, 2d, J 6.5 Hz for both), 1.20 (3 H, s), 2.23 (3 H, s), 2.67 and 3.34 (1 H, 2 quintets in a ratio of 5:1, respectively, J 6.5 Hz for both). ^{1}H NMR (1,3,3,5,5-pentamethylbicyclo[2.1.0]pentan-2-one) (60 MHz, CCl_4): δ 0.86 (3 H, s), 0.97 (3 H, s), 1.10 (4 H, s), 1.25 (3 H, s), 1.98 (3 H, s). MS of the isomeric mixture [IP 70 eV; *m/e* (% rel.int.)]: 153 (5, M), 152 (58, M), 137 (18, [M−CH_3]), 135 (33), 109 (54), 107 (31), 97 (100, [M−C_4H_7]), 91 (24), 81 (33), 79 (10), 71 (14), 69 (27), 67 (33), 55 (23), 53 (16), 43 (95).

An ethereal solution of a mixture of ketones *10–13* was treated with an excess of thiophenol at room temperature for 18 h.[22] Evaporation of the solvent left a yellow residue which distilled at 89–90 °C/0.01 mmHg to yield an isomeric mixture of isobutyryldimethylphenylthiocyclobutane derivatives *14* and *15*. Anal. $C_{16}H_{22}OS$: C, H. ^{1}H NMR (60 MHz, CCl_4): δ 0.55–3.78 (16H, extremely complex m), 4.43–5.27 (1 H, 3 separate m), 7.00–7.54 (5 H, m). IR (film): 3050 (w), 1698 (s), 1585 (m), 1480 (m), 1440 (m), 1378 (m), 1085 (m), 1023 (m), 735 (s), 688 (s) cm^{-1}. GLC analysis (15 % QFl, 150 °C) revealed the presence of at least five compounds. MS [IP 70 eV; *m/e* (% rel. int.)]: 262 (11, M), 191 (13, [M−C_4H_7O]), 153 (2, [M−PhS]), 152 (1, [M−PhSH]), 127 (44), 110 (15, PhSH), 109 (6, PhS), 85 (18), 83 (13), 81 (14), 71 (39, C_4H_7O), 69 (32), 55 (20) 43 (100, C_3H_7).

2-Acetyl-1,1-dibromo-2,3,3-trimethylcyclopropane (16) was treated with methyllithium according to method A and subsequently with an excess of thiophenol. Distillation followed by CC (silica gel, dichloromethane) afforded a mixture of acetyldimethylphenylthiocyclobutane derivatives *17* and *18*, b.p. 85–87 °C/0.02 mmHg. Due to limited stability the isomeric mixture was not obtained pure enough for elemental analysis. ^{1}H NMR (60 MHz, CCl_4): δ 1.15–2.65 (12 H, complex m comprising singlets in different positions), 4.47 and 5.15–5.28 (1 H, broad s and m, respectively), 7.02–7.58 (5 H, m). IR (film): 3050 (w) 1710 (s), 1600 (m), 1580 (m), 1480 (s), 1440 (s), 1095 (s), 1020 (m), 745 (s), 685 (s) cm^{-1}. MS [IP 70 eV; *m/e* (% rel. int.)]: 234 (35, M), 233 (65, [M−H]), 219 (9, [M−CH_3]), 191 (9, [M−Ac]), 163 (76), 149 (24), 125 (14, [M−PhS]), 124 (11, [M−PhSH]), 110 (100, PhSH), 109 (94, PhS), 82 (12, [M−PhS−Ac]), 81 (45).

Methyl 2,2-dibromo-1-methylcyclopropanecarboxylate (19) reacted with methyllithium under different conditions.

a. When the reaction was carried out at −78 °C according to method A a mixture of four products (from GLC [10 % QFl, 140 °C]) was isolated in 35 % yield, b.p. 27–28 °C/0.85 mmHg. The compounds were separated by preparative GLC (same conditions). The main product, comprising 80$_4$% of the mixture, was shown to be *2E*.[18]

b. When the reaction was carried out according to method A at −115 °C nine products were obtained. Distillation afforded a mixture of three products in approximately 30 % yield, b.p. 40–45 °C/1 mmHg. The components were separated by preparative GLC (15 % QFl, 150 °C) and identified as follows: (a) 20 % of the product mixture was shown to be methyl (*E*)-2-bromo-1-methylcyclopropanecarboxylate (*20E*),[38] (b) 50 % methyl (*Z*)-2-bromo-1-methylcyclopropanecarboxylate (*20Z*),[38] (c) 30 % methyl (*Z*)-2-bromo-1,2-dimethylcyclopropanecarboxylate (*21*). Anal. $C_7H_{11}BrO_2$: C, H. ^{1}H NMR (60 MHz, CCl_4): δ 0.80 (1 H, d, J 6.5 Hz), 1.37 (3 H, s), 1.85 (3 H, s), 1.93 (1 H, d, J 6.5 Hz), 3.70 (3 H, s). IR (film): 3060 (w) 3020 (m, shoulder), 1730 (s), 1455 (m), 1435 (s), 1385 (m), 1335 (m), 1305 (s), 1280 (s), 1200 (s), 1135 (s), 1000 (w), 875 (m), 865 (m), 810 (m), 775 (m), 730 (w), 465 (m) cm^{-1}.

Preparation of 2-(2-bromo-1-methylcyclopropyl)propan-2-ol (5). Alcohol *5* was prepared in 96 % yield by treatment of 2-acetyl-1-bromo-2-methylcyclopropane (*2*) (*E*/*Z* = 65/35 from NMR) with methyllithium at −78 °C according to method A, b.p. 43–44 °C/1.0 mmHg. Anal. $C_7H_{13}BrO$: C, H. The spectral data are not in complete accordance with those published by Barlet.[15] ^{1}H NMR (60 MHz, CCl_4): δ 0.50 and 0.87 (1 H, 2dd in a ratio of 61:39, respectively, J 4.5 and 6 Hz and J 6 and 8.5 Hz, respectively), 1.00–1.73 (11 H, m with main peaks at 1.10, 1.23 and 1.43), 2.86 and 3.20 (1 H, 2dd in a ratio of 37:63, respectively, J 4.5 and 8.5 Hz for both). IR (film): 3480 (m), 1378 (m), 1368 (m), 1120 (m), 955 (m) cm^{-1}. The isomeric composition was confirmed by GLC (20 % SE30, 135 °C).

REFERENCES

1. Taylor, K. G. and Hobbs, W. E. *Tetrahedron Lett.* (1968) 1221.
2. Taylor, K. G., Hobbs, W. E. and Saquet, M. *J. Org. Chem. 36* (1971) 369.

3. Baird, M. S. *Chem. Commun.* (1971) 1145.
4. Taylor, K. G., Hobbs, W. E., Clark, M. S. and Chaney, J. *J. Org. Chem. 37* (1972) 2436.
5. Taylor, K. G. and Chaney, J. *J. Am. Chem. Soc. 94* (1972) 8924.
6. Taylor, K. G. and Chaney, J. *J. Am. Chem. Soc. 98* (1976) 4158.
7. Taylor, K. G., Chaney, J. and Deck, J. C. *J. Am. Chem. Soc. 98* (1976) 4163.
8. Damiano, J.-C., Luche, J.-L. and Crabbé, P. *Tetrahedron Lett.* (1976) 779.
9. Boswell, R. F. and Bass, R. G. *J. Org. Chem. 40* (1975) 2419.
10. Baird, M. S. and Kaura, A. C. *Chem. Commun.* (1976) 356.
11. Maurin, R. and Bertrand, M. *Bull. Soc. Chim. Fr.* (1972) 2349, and references therein.
12. Allan, A. R. and Baird, M. S. *Chem. Commun.* (1975) 172.
13. Nilsen, N. O., Sydnes, L. K. and Skattebøl, L. *Chem. Commun.* (1978) 128.
14. Sydnes, L. and Skattebøl, L. *Tetrahedron Lett.* (1975) 4603.
15. Barlet, R. *Tetrahedron Lett.* (1976) 4171.
16. Sydnes, L. K. *Acta Chem. Scand. B 31* (1977) 823.
17. Skattebøl, L. *Acta Chem. Scand. 17* (1963) 1683.
18. Stein, C. A. and Morton, T. H. *Tetrahedron Lett.* (1973) 4933.
19. Sydnes, L. K. *Acta Chem. Scand. B 32* (1978) 47.
20. de Wolfe, W. H., Stol, W., Landheer, I. J. and Bickelhaupt, F. *Recl. Trav. Chim. Pays-Bas 90* (1971) 405.
21. Conia, J.-M. and Gore, J. *Bull. Soc. Chim. Fr.* (1963) 726.
22. Skattebøl, L. *Tetrahedron Lett.* (1970) 2361.
23. Kirmse, W. *Carbene Chemistry*, Academic, New York 1971.
24. Köbrich, G. and Goyert, W. *Tetrahedron 24* (1968) 4327.
25. Walborsky, H. M. and Motes, J. M. *J. Am. Chem. Soc. 92* (1970) 2445, and references therein.
26. Braun, M. and Seebach, D. *Angew. Chem. 86* (1974) 279.
27. Marquis, E. T. and Gardner, P. D. *Chem. Commun.* (1966) 726.
28. Kitatani, K., Hiyama, T. and Nozaki, H. *J. Am. Chem. Soc. 97* (1975) 949.
29. Kitatani, K., Hiyama, T. and Nozaki, H. *Bull. Soc. Chim. Jpn. 50* (1977) 3288.
30. Moore, W. R., Taylor, K. G., Müller, P., Hall, S. S. and Gaibel, Z. L. F. *Tetrahedron Lett.* (1970) 2365, and references therein.
31. Brown, D. W., Hendrick, M. E. and Jones, Jr., M. *Tetrahedron Lett.* (1973) 3951.
32. Reinarz, R. B. and Fonken, G. J. *Tetrahedron Lett.* (1974) 441.
33. Hamon, D. P. G. and Trenerry, V. C. *Tetrahedron Lett.* (1974) 1371.
34. Moore, W. R. and Hill, J. B. *Tetrahedron Lett.* (1970) 4343.
35. Paquette, L. A., Wilson, S. E., Henzel, R. P. and Allan, Jr., G. E. *J. Am. Chem. Soc. 94* (1972) 7761.
36. Reinarz, R. B. and Fonken, G. J. *Tetrahedron Lett.* (1973) 4013.
37. Kleveland, K. and Skattebøl, L. *Acta Chem. Scand. B 29* (1975) 827.
38. Sydnes, L., 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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