Chiral Organometallic Reagents, II[1]

Equilibration of Diastereomeric Carbenoids, the *tert*-Butyl 2-Bromo-2-lithio-1-methylcyclopropanecarboxylates

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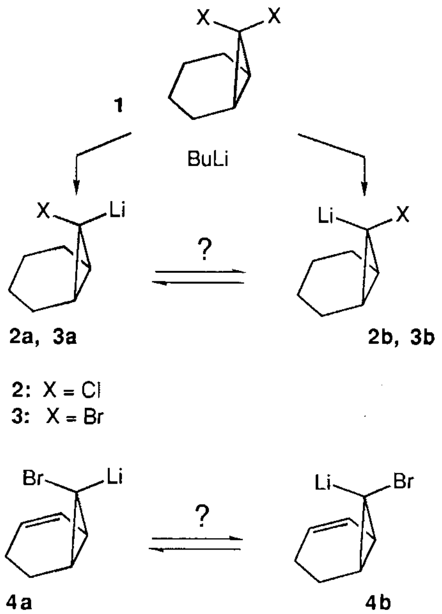
The diastereomeric carbenoids **6** are generated at −125°C from the dibromocyclopropane **5** by halogen-metal exchange and trapped by electrophiles. Since the resulting carbenoids **6** equilibrated by halogen-metal exchange with their precursor dibromo compound **5**, the product ratios depend strongly on the reaction conditions used. Normal addition of *n*-butyllithium favors equilibration giving "thermodynamic ratios" of the carbenoids. Inverse addition of **5** to *tert*-butyllithium approaches the "kinetic ratio" of carbenoids, which is revealed in reactions in which the carbenoids are trapped in situ by alcohols. The carbenoids **6** have been found to be configurationally stable at −125°C. They undergo rapid equilibration at temperatures above −78°C before decomposition sets in at −60°C.

As soon as carbenoids were recognized as bona fide α-halogeno-organolithium compounds[2] the question has been raised, whether these species are configurationally stable or not. The first careful studies suggested that the chloro carbenoid **2a** rearranges only slowly to its epimer **2b** at −80°C at a rate comparable to its decomposition[3].

Subsequent detailed studies by Seyferth[4,5] on the bromo carbenoids **3** have shown them to be configurationally stable at −95°C in THF or THF/ether mixtures. Epimerisation of **3a** to **3b** has been suggested by Warner[6] to occur only at or above −78°C. Likewise, the epimerisation of **4a** to **4b** has been postulated by Warner[7] to precede the Skattebol rearrangement[8] of **4a** having its onset at about −78°C in THF. While these results define the temperature range in which stereoisomeric carbenoids with a cyclopropane backbone can be handled, the use of these organometallics in synthesis requires defined routes to either stereoisomer of the carbenoids. In the case of **3a** and **3b** the problem has been solved by Seyferth[4,5,9] by transmetalation of the individual α-bromo-organotin compounds. A more attractive route would be to control the diastereoselectivity in the lithium-bromine exchange of the diastereotopic bromine atoms in **1** or related 1,1-dibromocyclopropanes.



For any study along these lines the observation of Seyferth[4,5] is most important, that the epimeric carbenoids **3** are equilibrated in a halogen-metal exchange reaction involving the dibromo compound **1** as a relay. It is hence easier to obtain the carbenoids **3** under thermodynamic than under kinetic control, a fact that has since been used by other workers in the field[7,10,11]. Since the diastereomeric carbenoids are partially equilibrated during their generation

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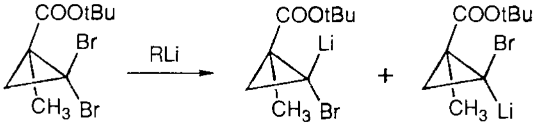
***) The work described here is based on the dissertation of A. Schmidt, Hannover 1976, the contents of which has not been published as a consequence of the untimely death of G. K. This thesis contains many results illuminating the problem of carbenoid generation and carbenoid reactions, results which should be made accessible to the other workers in the field. The results written up in this paper are, however, discussed in the context of our present-day understanding. For the state of the art in 1976 the reader should consult the original dissertation of A. S.

from the dibromo compound product ratios depend significantly on the procedural details of the generation of the carbenoids and their trapping (cf. e.g. ref.[10]). In the present study we show how changes in the metalating agent and in the order of addition of the reagents can affect the product ratios in the reaction of the dibromo compound **5**.

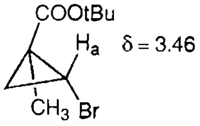
Induced Equilibration of the Diastereomeric Carbenoids 6

The substituted *tert*-butyl ester **5** is prepared by addition of dibromocarbene to methyl methacrylate followed by saponification[12] and reesterification by isobutene.

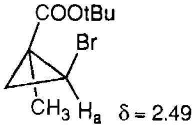


5 **6a** **6b**

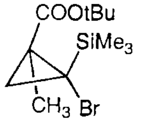
Bromine-lithium exchange is effected by treatment of **5** with 1.03 equivalents of *n*-butyllithium in a Trapp-solvent mixture[13] at −125 °C. The reaction is quenched after 30 min by the addition of an excess of solid methanol. This way, quenching can be effected without causing a rise in temperature. The products **7** are formed in 95% yield and a 78:22 ratio. Structural assignment rests on the 90-MHz ^{1}H-NMR spectra in which the proton H_A in the isomer **7a** resonates at lower field due to the influence of the neighboring carbonyl group[14]. Likewise trapping of the carbenoids **6** by chlorotrimethylsilane leads to 97% of the silyl derivatives **8** in a 77:23 ratio. Structural assignment in analogy to that of **7** is supported by a study of the Eu(fod)$_3$-induced chemical shifts in the ^{1}H-NMR spectra of the individual isomers. Carboxylation of the carbenoids **6** results in 89% yield of the acids **9** in a 80:20 ratio.



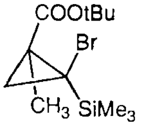
7a



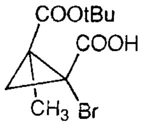
7b



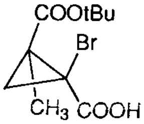
8a



8b



9a



9b

Thus, the product ratio has been found to be independent of the nature of the electrophile, which indicates that any equilibration of the diastereomeric carbenoids **6a** and **6b** must be significantly slower than the trapping reactions. These results do not reveal, however, whether some equilibration has occurred during the preparation of the carbenoids (cf. refs.[4,5]) or between generation and trapping. It has occurred to us that this may become apparent by generating the carbenoids via an "inverse addition" technique. If equilibration via the starting material **5** takes place, the lower concentration of **5** available to the carbenoids **6** during the inverse addition should lead to lesser equilibration and, hence, to a different product ratio than in the "normal addition" described above. Actually, such different product ratios for normal and inverse addition have been reported for the generation of **3**[5], but not commented. In fact, addition of the dibromo compounds **5** to *n*-butyllithium at −125 °C followed by quenching with methanol leads to **7a** and **7b** in a 59:41 ratio, clearly different from the one obtained by the normal addition route.

But even during the "inverse addition" of the dibromo compound **5** to the butyllithium some equilibration between the diastereomeric carbenoids mediated by **5** may occur, especially at times when substantial amounts of the carbenoid are already formed and the concentration of the remaining butyllithium becomes low. A better indication of kinetically controlled diastereoselection in the generation of the carbenoids of **6** from the dibromo compounds **5** would be obtained by in situ trapping of the carbenoids as they are formed. This technique has been applied by Nozaki's group[10,15] to the generation of the carbenoids **3** from **1** at −95 °C. A kinetic diastereoselection of ca. 4:1 favoring the exchange of the *endo*-bromine atom has been reported to be close to Seyferth's[4] value of 3.2:1 for the metalation at −124 °C. In our case, four equivalents of *n*-butyllithium are added at −125 °C to a 12:1 mixture of methanol and the dibromo compound **5** in a Trapp-solvent mixture. This results in a 33:67 ratio of the diastereomeric monobromo compounds **7**. If this represents or at least approximates the kinetic diastereoselection in the exchange of the diastereotopic bromine atoms of **5** it becomes clear that even during the inverse addition reaction a significant equilibration of the carbenoids mediated by **5** has occurred.

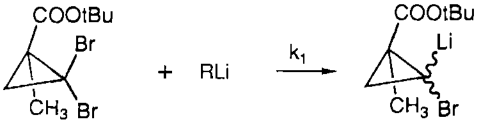
It is thus of interest to evaluate the efficiency of the in situ trapping, which is governed by the rate of protonation of the carbenoids **6** relative to the rate of their exchange reaction with the precursor **5**. If protonation is indeed faster than the latter process, the product ratio should be independent of the proton source used. To this end, additional

Table 1. In situ trapping of the carbenoids **6** by 12 equivalents of proton sources at −125 °C

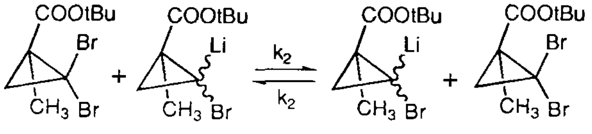
Proton source	Yield of 7 (%)	7a:7b	Recovered starting material (%)
H_2O	64	36:64	25
MeOH	55	33:67	37
*t*BuOH	35	34:66	63
DMSO	81	42:58	10

in situ trapping experiments have been carried out with water, *tert*-butyl alcohol and DMSO. The data in Table 1 show that the hydroxy group-containing acids lead to practically identical product ratios. This suggests that in situ trapping is indeed faster than the equilibration, and that the 34:66 ratio represents the kinetic diastereoselection in the generation of the carbenoids **6** from **5**. On the other hand, DMSO as a proton source protonates the carbenoids **6** more slowly, so that equilibration becomes noticeable.

The factors that limit or lead to kinetic diastereoselection in the halogen-metal exchange on the dibromo compound **5** are now recognized to be the relative rates of two halogen-metal exchange processes:



5 **6** (1)



5 **6** **6** **5** (2)

The faster the reaction (1) is, compared with reaction (2), the more closely the product ratio represents the kinetic diastereoselection in step (1). While the rate of reaction (2) cannot be manipulated, that of reaction (1) certainly should depend on the reagent RLi used. This has opened an additional possibility to improve kinetic diastereoselection in the halogen-metal exchange of the dibromo compound **5**. The results of experiments using *tert*-butyllithium and phenyllithium are compared with those obtained with *n*-butyllithium in Table 2.

Table 2. Diastereoselectivity in the generation and trapping of the carbenoids **6** as a function of the metalating agent at −125°C

Metalating agent	"Inverse addition" Yield (GC)	"Inverse addition" **7a**:**7b**	"Normal addition" Yield (GC)	"Normal addition" **7a**:**7b**
*t*BuLi	95%	38:62	93	64:36
PhLi	94%	54:46	(101)	63:36
*n*BuLi	93%	59:41	95	78:22

In line with the expectation that *tert*-butyllithium is more reactive in the halogen-metal exchange reaction than *n*-butyllithium, the 38:62 ratio found in the inverse addition process approximates quite closely the values representing kinetic diastereoselection (cf. Table 1). This is to be compared with the corresponding reaction of *n*-butyllithium which, as discussed before, allows for partial equilibration of the carbenoids. Phenyllithium occupies an intermediate position. *tert*-Butyllithium and phenyllithium are also more effective than *n*-butyllithium in undercutting the equilibration between the diastereomeric carbenoids **6** in the experiments carried out by the "normal" addition mode.

The data in Table 2 give also a clue as to whether the carbenoids **6** equilibrate in the absence of their precursor **5** over the 30-min period between generation and quenching by methanol at −125°C. If this was the case, all the product ratios in Table 2 would be identical. Thus, these results attest the now well-known fact[4,6,7,9)] that carbenoids with a cyclopropane backbone are configurationally stable at low temperatures. But is there a temperature range, in which the carbenoids such as **6** equilibrate thermally before decomposition occurs?

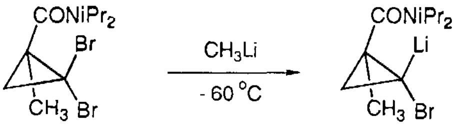
Thermal Equilibration of the Diastereomeric Carbenoids 6

The thermal equilibration of the carbenoids **6** is certainly limited by their thermal instability. In order to define the temperature range in which the carbenoids **6** can be handled, they are generated at −125°C, then warmed rapidly to a specified temperature, kept for 15 min and quenched by addition of either methanol or chlorotrimethylsilane. The total sum of carbenoid derived low molecular weight products is taken as an indication of the amount of carbenoids available. In this way it is found that **6** generated by the "normal" addition of *n*-butyllithium is stable (>90%) at −58°C for 15 min. **6** generated analogously with *tert*-butyllithium appears to be more labile; thus, only ca. 70% of **6** survive. Likewise, carbenoid **6** formed by inverse addition to *tert*-butyllithium survives to ca. 75% at −58°C for 15 min. In the latter two cases >90% stability is observed at −78°C (cf. Figures 1a−c).

The ratio of the diastereomeric carbenoids **6** changed with temperature in a twofold manner. In the low-temperature range there is a clear tendency of **6a** to isomerize to **6b**. This is not seen in Figure 1c in which the **6a**:**6b** ratio is 38:62 in the beginning, i.e. being closer to the estimated equilibrium value of the low temperature region.

There is at and above −78°C the high-temperature region (Figures 1b and 1c), in which the carbenoids approach an equilibrium favoring the *cis*-isomer **6a** to about 95:5. This trend is not seen in Figure 1a but if the carbenoids generated in the normal way with *n*-butyllithium are tempered at −58°C (cf. Figure 2), the tendency to favor **6a** at equilibrium also becomes apparent at the onset of the thermal decomposition.

The effects occurring in the high-temperature region are those expected from the results in the foregoing section where equilibration of **6** via the dibromo compound **5** leads to a preponderance of the *cis*-carbenoid **6a**. This seems reasonable, since in **6a**, but not in **6b**, the lithium can be stabilized by internal coordination of the carbonyl group. A similar effect has been discussed[12)] for the corresponding



10 **11**

carbenoids **11**, the exclusive product from the reaction of the dibromo compound **10** with methyllithium. One may speculate that the selective generation of **11** represents a thermodynamic control of diastereoselectivity.

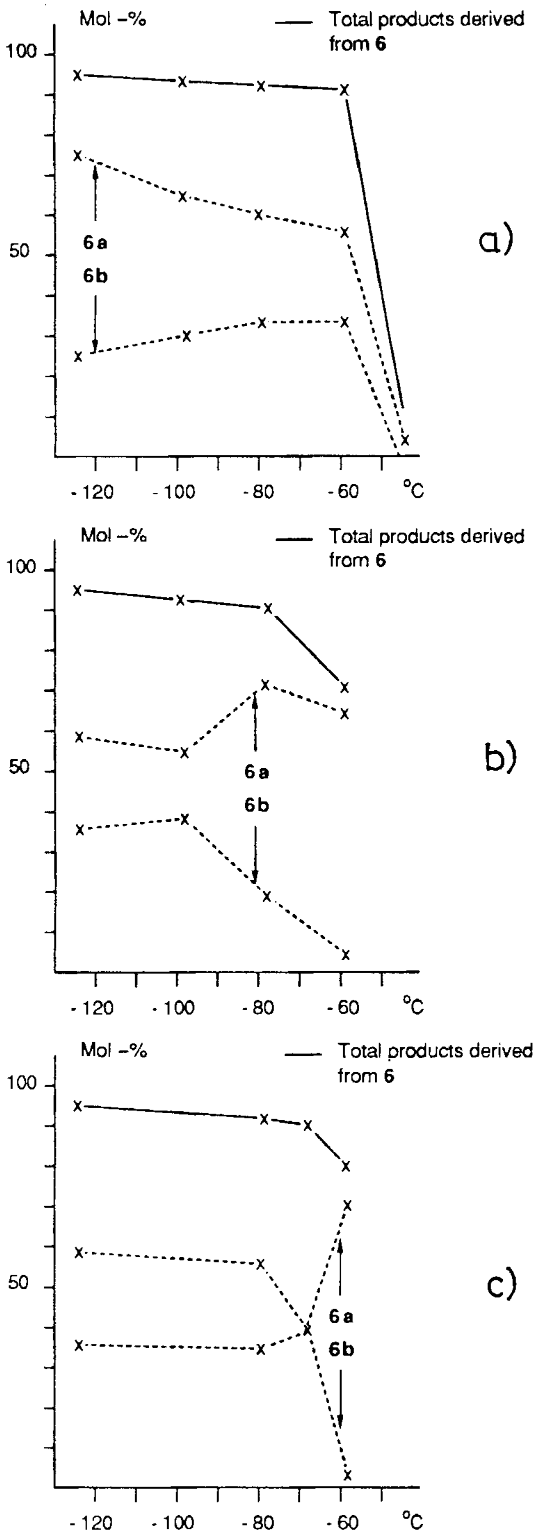


Figure 1. Equilibration of the carbenoids **6** by stirring for 15 min at the indicated temperatures. – a) **6** generated with *n*BuLi. – b) **6** generated with *t*BuLi. – c) **6** generated with *t*BuLi "inverse"

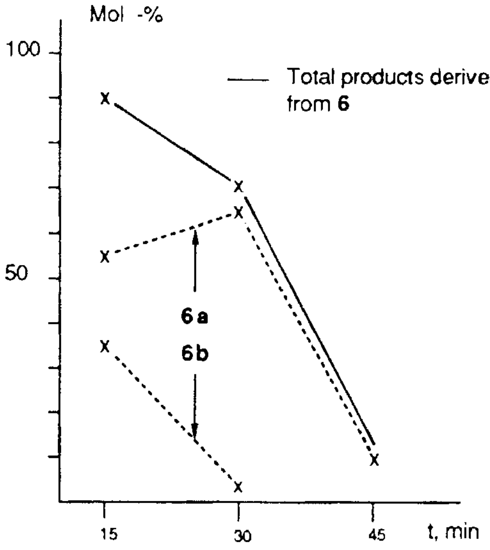


Figure 2. Equilibration of the carbenoids **6** at –58°C (generated with *n*BuLi)

More surprising is the behavior of the carbenoids **6** in the "low-temperature" region, seen in Figures 1a and 1b and which prevails also in Figure 1c. We can not offer any explanation for this at present and refer to the universal excuse of "aggregation phenomena".

In summary the kinetic diastereomer ratio of the carbenoids **6** generated from the dibromo compound **5** is revealed by in situ trapping with alcohols or by the inverse generation using *tert*-butyllithium. The carbenoids equilibrate by a process mediated by their precursor dibromo compound. In the absence of this precursor the carbenoids are configurationally stable at –120°C. At higher temperatures, especially above –78°C (thermal?) equilibration occurs by as yet unknown mechanisms.

R. W. H. expresses his thanks to Prof. *E. Winterfeldt*, Hannover, for making the thesis of A.S. available to him.

Experimental

All temperatures quoted are uncorrected. – ^{1}H NMR: Bruker HX 90. – Analytical gas chromatography: Varian Aerograph 1400 with Varian Aerograph 477 integrator, carrier gas N_2. – Preparative gas chromatography: Wilkens A700, carrier gas H_2.

1. *tert-Butyl 2,2-Dibromo-1-methylcyclopropanecarboxylate* (**5**): Into a 0.5-l glas-pressure bottle was added at –78°C 70 g (ca. 270 mmol) of crude 2,2-dibromo-1-methylcyclopropanecarboxylic acid[12], 100 ml of anhydrous ether, 200 ml of isobutene, and 5 ml of conc. sulfuric acid. The bottle was closed and shaken at room temp. for 3 h. The bottle was recooled to –78°C, and the contents were stirred into a solution of 60 g (0.43 mol) of potassium carbonate in 100 ml of water and 100 g of ice. During the addition the aqueous phase should remain alkaline. The phases were separated, and the aqueous phase was extracted five times with 50 ml each of ether. The combined organic phases were dried with potassium carbonate. While the solution was concentrated in vacuo small amounts of freshly ground potassium carbonate were added. The crude ester was vacuum-distilled from potassium carbonate in glassware pretreated with sodium hydroxide. Distillation was com-

menced at −20°C; upon slowly raising the temperature 60.5 g (71%) of **5** was obtained with b.p. 74°C/0.15 Torr. The material was stored in the dark at −20°C up to one week, otherwise, it was freshly redistilled as described above. — ^{1}H NMR (90 MHz, C_6D_6): δ = 1.00 (d, *J* = 7.5 Hz, 1H), 1.30 (s, 9H), 1.31 (s, 3H), 2.19 (d, *J* = 7.5 Hz, 1H).

$C_9H_{14}Br_2O_2$ (314.0)
Calcd. C 34.42 H 4.49 Br 50.89
Found C 34.37 H 4.56 Br 50.69

2. *Generation of the Carbenoids* **6**: Into a carefully dried three-necked flask equipped with a stirrer, thermometer, and dropping funnel was added under nitrogen 4.5 mmol of *tert*-butyl 2,2-dibromo-1-methyl-cyclopropane-carboxylate (**5**) (exactly weighed), ca. 450 mg of dodecane (exactly weighed), and 5 ml of petroleum ether (b.p. 40−60°C). 20 ml of THF was distilled from $LiAlH_4$ directly into the dropping funnel. The THF was added to the flask followed by addition of 5 ml of anhydrous ether. After cooling to −125°C 1.03 equivalents of a ca. 0.8 M solution of n-butyllithium in ether were added dropwise over 20 min. Subsequently 2 ml of petroleum ether (b.p. 40−60°C) was added through the same dropping funnel. The resulting suspension containing **6** was stirred at −125°C for 30 min.

In the *in situ trapping* experiments 60 mmol of e.g. H_2O, CH_3OH, *t*BuOH, or DMSO was introduced into the flask at the beginning. In these reactions 4 equivalents of *n*-butyllithium in ether was added as described above. The resulting suspension was stirred for 30 min at −125°C.

For the *inverse addition*, the process is the same as in the first procedure, except that the dibromo compound (dissolved in 5 ml of ether) is added dropwise over 20 min to the precooled (−125°C) butyllithium solution (1.03 equivalents). The resulting suspension was stirred for 30 min at −125°C.

3. *tert-Butyl 2-Bromo-1-methylcyclopropanecarboxylates* (**7**): 1 ml of methanol was cooled in a reagent tube in liquid nitrogen. The reagent tube was quickly smashed, and the solid methanol was added to the suspension prepared according to procedure 2. After stirring for 20 min the mixture was allowed to reach room temperature. Quantitative gas chromatography on a 2-m column with 5% QF1 on Chromosorb G revealed the presence of 74.15% of **7a** and 21.03% of **7b** determined relative to internal dodecane. The mixture was transferred to a separation funnel, the flask was washed twice with 50 ml of ether and then with water. After mixing the phases, the aqueous phase was extracted twice with 50 ml of ether. The combined organic phases were dried with $MgSO_4$ and concentrated. The esters were separated by preparative GC on a 3-m column with 30% QF1 on Chromosorb G, 140°C.

(1*R**,2*S**)-(**7a**): ^{1}H NMR (90 MHz, C_6D_6): δ = 0.63 (dd, *J* = 5.1 and 5.8 Hz, 1H), 1.24 (s, 9H), 1.40 (s, 3H), 1.57 (dd, *J* = 5.8 and 8.1 Hz, 1H), 3.46 (dd, *J* = 5.1 and 8.1 Hz, 1H).

(1*R**,2*R**)-(**7b**): ^{1}H NMR (90 MHz, C_6D_6): δ = 0.61 (dd, *J* = 6.5 and 7.5 Hz, 1H), 1.01 (s, 3H), 1.39 (s, 9H), 1.72 (dd, *J* = 5.5 and 6.5 Hz, 1H), 2.49 (dd, *J* = 5.5 and 7.5 Hz, 1H).

$C_9H_{15}BrO_2$ (235.1)
Calcd. C 45.98 H 6.43 Br 33.99
7a: Found C 45.75 H 6.35 Br 33.84
7b: Found C 45.82 H 6.49 Br 33.62

4. *tert-Butyl 2-Bromo-1-methyl-2-(trimethylsilyl)cyclopropanecarboxylates* (**8**): 1.5 ml (ca. 11 mmol) of chlorotrimethylsilane was added to the carbenoids **6** generated as described under 2. After stirring at −125°C for 30 min the mixture was allowed to reach room temperatur. Quantitative GC analyses on a 2-m column with 5% Carbowax 20 M on Chromosorb G showed the presence of 74.5% of **8a** and of 22.8% of **8b**. The mixture was worked up as described under 3, and the esters were separated by preparative GC on a 3-m column with 5% Carbowax 20 M at 152°C.

(1*R**,2*S**)-**8a**: ^{1}H NMR (90 MHz, C_6D_6): δ = 0.27 (s, 9H), 0.92 (d, *J* = 6.5 Hz, 1H), 1.29 (s, 9H), 1.60 (s, 3H), 1.70 (d, *J* = 6.5 Hz, 1H).

(1*R**,2*R**)-**8b**: ^{1}H NMR (90 MHz, C_6D_6): δ = 0.12 (s, 9H), 0.75 (d, *J* = 6.5 Hz, 1H), 1.29 (s, 3H), 1.44 (s, 9H), 2.05 (d, *J* = 6.5 Hz, 1H).

$C_{12}H_{23}BrO_2Si$ (307.3)
Calcd. C 46.90 H 7.54 Br 26.00
8a: Found C 47.22 H 7.36 Br 25.80
8b: Found C 47.15 H 7.30 Br 25.85

5. *Methyl 1-Bromo-2-(tert-butoxycarbonyl)-2-methylcyclopropanecarboxylate:* Dry ice was pulverized and recooled in liquid nitrogen. An excess of this solid CO_2 was added to the carbenoids **6** generated as described under 2. After stirring for 1 h the mixture was allowed to reach room temp. and transferred to a separating funnel. The flask was rinsed twice with 50 ml of ether and with water. A few milliliters of 2 N aqueous NaOH was added, and the phases were separated after vigorous shaking of the mixture. The aqueous phase was washed twice with 50 ml of ether. The aqueous phase was subsequently acidified with 2 N H_2SO_4 and extracted five times with 50 ml each of ether. The combined extracts were dried with $MgSO_4$ and treated with an ethereal diazomethane solution. After concentration the yields of the diesters corresponding to **9** were determined by quantitative GC on a 2-m column with 5% SE30. The ratio of the esters was determined by ^{1}H-NMR spectroscopy establishing the presence of 71% of the ester corresponding to **9a** and 18% of the ester corresponding to **9b**. 2.0 g of the crude ester was separated by chromatography over a 80 cm × 3 cm column filled with silica gel (0.05−0.2 mm, Woelm) by using petroleum ether (40−60°C)/ether (98:2) as the eluent.

Methyl Ester of (1*R**,2*S**)-**9a**: ^{1}H NMR (90 MHz, C_6D_6): δ = 0.84 (d, *J* = 6.5 Hz, 1H), 1.26 (s, 9H), 1.42 (s, 3H), 2.27 (d, *J* = 6.5 Hz, 1H), 3.35 (s, 3H).

Methyl Ester of (1*R**,2*R**)-**9b**: ^{1}H NMR (90 MHz, C_6D_6): δ = 1.27 (s, 3H), 1.37 (s, 9H), 1.66 (d, *J* = 6.5 Hz, 1H), 1.97 (d, *J* = 6.5 Hz, 1H), 3.28 (s, 3H).

$C_{11}H_{17}BrO_4$ (293.2)
Calcd. C 45.07 H 5.85 Br 27.26
Ester of **9a**: Found C 45.23 H 5.86 Br 27.15
Ester of **9b**: Found C 45.08 H 5.90 Br 27.20

CAS Registry Numbers

5 (acid): 5365-21-9 / **5**: 132259-74-6 / **6a**: 132259-75-7 / **6b**: 132259-76-8 / **7a**: 132259-77-9 / **7b**: 132259-78-0 / **8a**: 132259-79-1 / **8b**: 132259-80-4 / **9a**: 132259-81-5 / **9b**: 132259-82-6 / isobutene: 115-11-7

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[1] For Part I see: R. W. Hoffmann, M. Bewersdorf, M. Krüger, W. Mikolaiski, R. Stürmer, *Chem. Ber.* **124** (1991) 1243, preceding paper.

[2] G. Köbrich, *Angew. Chem.* **79** (1967) 15; *Angew. Chem. Int. Ed. Engl.* **6** (1967) 41.

[3] G. Köbrich, W. Goyert, *Tetrahedron* **24** (1968) 4327.

[4] D. Seyferth, R. L. Lambert, jr., *J. Organomet. Chem.* **55** (1973) C 53.

[5] D. Seyferth, R. L. Lambert, jr., M. Massol, *J. Organomet. Chem.* **88** (1975) 255.

[6] P. M. Warner, S.-C. Chang, N. J. Koszewski, *Tetrahedron Lett.* **26** (1985) 5371.

[7] P. M. Warner, R. D. Herold, *J. Org. Chem.* **48** (1983) 5411.

[8] [8a] L. Skattebol, *Tetrahedron* **23** (1967) 1107. – [8b] G. Boche, H. M. Walborsky, *Cyclopropane-Derived Reactive Intermediates*, p. 449, J. Wiley, New York 1990.

[9] D. Seyferth, R. L. Lambert, jr., *J. Organomet. Chem.* **88** (1975) 287.

[10] K. Kitatani, T. Hiyama, H. Nozaki, *Bull. Chem. Soc. Jpn.* **50** (1977) 3288.

[11] [11a] T. Harada, K. Hattori, T. Katsuhira, A. Oku, *Tetrahedron Lett.* **30** (1989) 6035. – [11b] A. Weber, R. Galli, G. Sabbioni, U. Stämpfli, S. Walther, M. Neuenschwander, *Helv. Chim. Acta* **72** (1989) 41.

[12] M. S. Baird, A. G. W. Baxter, *Chem. Soc., Perkin Trans. 1*, **1979**, 2317.

[13] G. Köbrich, H. Trapp, *Chem. Ber.* **99** (1966) 670.

[14] [14a] D. J. Patel, M. E. H. Howden, J. D. Roberts, *J. Am. Chem. Soc.* **85** (1963) 3218. – [14b] A. A. Pavia, J. Wylde, R. Wylde, E. Arnal, *Bull. Soc. Chim. Fr.* **1965**, 2709.

[15] K. Kitatani, T. Hiyama, H. Nozaki, *J. Am. Chem. Soc.* **97** (1975) 949.

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