# Stereoselective Monoalkylation of α-Halocyclopropyllithiums. A Versatile Method for the Synthesis of α-Alkylcyclopropyl Acetates and Alkylidenecyclopropanes

Katuzi KITATANI, Tamejiro HIYAMA, and Hitosi NOZAKI
*Department of Industrial Chemistry, Kyoto University, Yoshida, Kyoto 606*
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The title carbenoids (**7** and **8**) prepared by the action of butyllithium on dihalocyclopropanes are smoothly methylated with methyl iodide. The product ratio of *cis*-methylated product (**3**)/*trans*-methylated one (**4**) (or *endo*-methylated product (**5**)/*exo*-methylated one (**6**) is found to depend on the aging period of the carbenoids; thermodynamic equilibration gives almost **3** or **5**. This procedure has been extended to general alkylation by utilizing HMPA co-solvent. The resulting α-alkylated cyclopropyl halides are converted into allylic acetates or cyclopropyl acetates upon acetolysis and also into alkylidenecyclopropanes upon base treatment. The protonolysis of **8** gives *trans*- or *exo*-bromocyclopropanes stereoselectively.

Halogen-metal exchange of *gem*-dihalo compounds with alkyllithium occurs easily to give lithium carbenoids which are generally nucleophilic enough to react with various electrophiles at low temperatures.[1] The title carbenoids derived from olefin-dihalocarbene adducts are thermally labile and decompose above −50 °C.[2] This instability has restricted their synthetic use only to such intramolecular process leading to allene and/or bicyclobutane formation.[3] As lithiation of *gem*-dihalocyclopropanes proceeds rapidly even at sufficiently low temperature (*e.g.* −110 °C) and the resulting carbenoids are stable for several hours to exist as such at −95 °C,[4] we have studied to utilize the reactive intermediates for synthetic purpose and found these species can actually add to carbonyl compounds, affording cyclopropyl ketones, cyclobutanones or 1,1-cyclopropanedicarboxylates.[5] This article describes alkylation of the carbenoids and several transformations of the resulting α-alkylcyclopropyl halides.[6]

*Alkylation of α-Halocycloprophyllithiums.* The carbenoids generated by lithiation of *gem*-dibromocyclopropanes (**1** or **2**) at −95 °C with butyllithium were converted into α-alkylcyclopropyl bromides in good yields upon treatment with excess alkyl halides. Methylation was scrutinized first in the hope that the present reaction would provide a short-cut methodology to construct a methyl substituted cyclopropane moiety commonly found among various natural products.[7] The results are summarized in Table 1. Addition of methyl iodide after 10 minutes' aging of the carbenoids (conditions A) resulted in the exclusive or at least predominant formation of *cis*-methylated products **3** or *endo*-methylated ones **5**. This might be ascribed to the thermodynamically preferred configuration of the carbenoid. When methyl iodide is present at the stage of lithium-halogen exchange, the resulting carbenoid should be methylated spontaneously before the configurational isomerization of the carbenoid (conditions B). The experiments showed a little increase of *trans*-methylated isomers **4** or *exo*-methylated ones **6**. Furthermore, the use of hexamethylphosphoric triamide (HMPA) co-solvent is expected to prompt the alkylation (conditions C). These conditions may reflect to some extent the susceptibility of each geminal bromine atom to the lithium-bromine exchange. The products were obtained in better yields with almost the same isomer ratio as conditions B, in general, with the exception of the reaction of **1a**, which yielded the otherwise less favored isomer **4a** now predominantly.

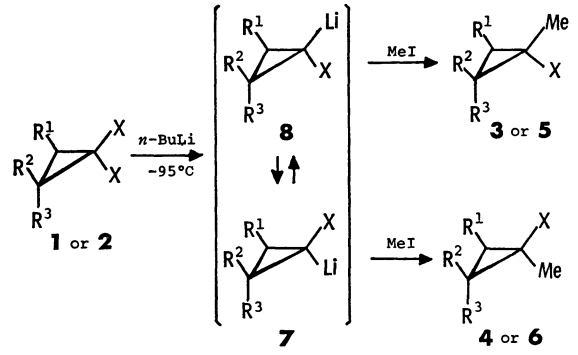
These observations can be understood by the Scheme 1. Less hindered bromine atom is preferentially lithiated to give a carbenoid **7** which isomerizes to thermodynamically more stable isomer **8**.[8] Subsequent methylation of **8** and **7** proceeds with retention of configuration to yield **3** (or **5**) and **4** (or **6**) respectively. The exclusive formation of **3** or **5** under the conditions A may be attributed to complete isomerization of **7** to **8**. The exclusive formation of **3c** from **1c** is particularly attributable to the ethereal substituent.[9]

In contrast, however, methylation of 1,1-dichloro-2-phenylcyclopropane (**1d**) afforded **3f** and **4f** with 12: 88 ratio under the conditions A, possibly due to slow configurational isomerization of the intermediary car-

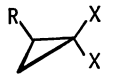
Table 1. Yield (%) of the products in the methylation of 1,1-dibromocyclopropanes and the product ratios (**3**: **4** or **5**: **6**)

| Dibromocyclopropane | Products | Conditions[a] A | B | C |
|---|---|---|---|---|
| **1a** | **3a**+**4a** | 70(100: 0) | 92(75: 25) | 90(38: 62) |
| **1b** | **3b**+**4b** | 66(88: 12) | 80(77: 23) | 72(78: 22) |
| **1c** | **3c**+**4c** | 89(100: 0) | 73(63: 37) | 92(77: 23) |
| **2a** | **5a**+**6a** | 60(100: 0) | 67(81: 19) | 86(80: 20) |
| **2b** | **5b**+**6b** | 55(100: 0) | 59(89: 11) | 99(78: 22) |

a) Details given in the Experimental part.

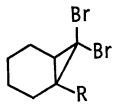



Scheme 1.



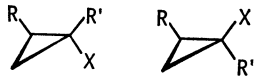
1

**a**, R=Ph, X=Br
**b**, R=*n*-$C_6H_{13}$, X=Br
**c**, R=$PhCH_2OCH_2$, X=Br
**d**, R=Ph, X=Cl



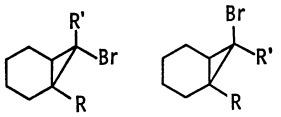
2

**a**, R=H
**b**, R=Me



3 4

**a**, R=Ph, R′=Me, X=Br
**b**, R=*n*-$C_6H_{13}$, R′=Me, X=Br
**c**, R=$PhCH_2OCH_2$, R′=Me, X=Br
**d**, R=Ph, R′=$CH_2$=$CHCH_2$, X=Br
**e**, R=Ph, R′=Et, X=Br
**f**, R=Ph, R′=Me, X=Cl
**g**, R=Ph, R′=H, X=Br
**h**, R=*n*-$C_6H_{13}$, R′=H, X=Br
**i**, R=$PhCH_2OCH_2$, R′=H, X=Br
**j**, R=Ph, R′=H, X=Cl



5 6

**a**, R=H, R′=Me
**b**, R=Me, R′=Me
**c**, R=H, R′=$CH_2$=$CHCH_2$
**d**, R=H, R′=$Me_2C$=$CHCH_2$
e, R=H, R′=H
**f**, R=Me, R′=H

benoids.[10]

Alkylation with ethyl iodide or allyl bromide required modification of the reaction conditions. Both halides turned out to react sluggishly. The use of HMPA co-solvent was found indispensable in order to eliminate the possible decomposition of carbenoids during the long reaction time. Another complicating side reaction was elimination of hydrogen halide from alkyl halides having β-hydrogen. This was, however, successfully suppressed by the addition of copper(I) salt such as copper(I) iodide or phenylacetylide.[11] Thus, **1a** was converted to **3d** and **4d** (89: 11, 59% yield) and to **3e** and **4e** (94: 6, 54% yield) respectively in the presence of Cu(I). Noteworthy is the alkylation of 7,7-dibromonorcarane with allyl bromide or 3-methyl-2-butenyl bromide; *endo*-alkylated product **5c** (87%) or **5d** (77%) was obtained exclusively. It should be noted that the coupling of 3-methyl-2-butenyl bromide with the carbenoid occurred at the α-position and no trace of $S_N2'$ product was detected.

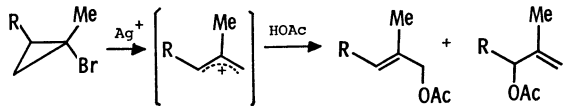
*Stereoselective Reduction of* gem-*Dihalocyclopropanes.* Protonolysis of the carbenoids, prepared as above, is expected to give monohalocyclopropanes[12] with high degree of stereoselectivity. Thus, production of the carbenoids according to the conditions A and the successive workup with ethanol at low temperature afforded monohalocyclopropanes (Table 2), the stereoselectivity being comparable with the above alkylation.

Table 2. Stereoselective reduction of 1,1-dihalocyclopropanes

| Dihalocyclopropane | Products (yield, %)[a] | Product ratio[b] (**3**: **4** or **5**: **6**) |
|---|---|---|
| **1a** | **3g**(87) | 100: 0 |
| **1b** | **3h**+**4h**(75) | 81:19 |
| **1c** | **3i**(83) | 100: 0 |
| **1d** | **3j**+**4j**(82) | 26:74 |
| **2a** | **5e**(90) | 100: 0 |
| **2b** | **5f**+**6f**(74) | 92: 8 |

a) Isolated yield after short-path distillation. b) The isomer ratio was calculated by GLC or NMR assay.

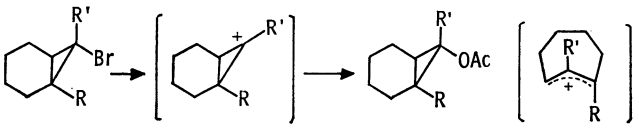
*Acetolysis of α-Alkylcyclopropyl Bromides.* The well-known conversion of monohalocyclopropanes into allyl cations obeys the orbital symmetry rule.[13] Therefore, α-alkylcyclopropyl halides obtained selectively should be utilized for selective olefin synthesis. We have attempted the acetolysis of **3** and **5** by heating in acetic acid in the presence of silver acetate and a catalytic amount of silver tetrafluoroborate. The bromocyclopropane **3a** gave 2-methyl-3-phenyl-2-propen-1-yl acetate (**9a**) in 74% yield and no regioisomer **10a**. In contrast **3b** produced two isomeric acetates **9b** (32%) and **10b** (43%), while **3c** gave **9c** (30%) and **10c** (28%). The trisubstituted ethylenes **9a**—**c** were found to have E configuration and this was attributed to the energetically favorable W-form of cations **11**.



3 11 9 10

**a**, R=Ph **b**, R=*n*-$C_6H_{13}$ **c**, R=$PhCH_2OCH_2$

The *endo*-alkylated bromonorcaranes **5** unexpectedly underwent acetolysis and the products were proved to be 7-acetoxy-7-alkylnorcaranes **12**. The *exo* configuration of 7-acetoxyl group is based on the assumed $S_N1$ type reaction involving **13**, which is stabilized by 7-alkyl group and do not rearrange into the strained cycloheptenyl cation **14**, and also based on the approach control. Similar stabilization has been recorded by Ledlie *et al.*[14]

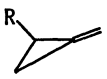


5 13 12 14

**a**, R=H, R′=Me 63%
**b**, R=Me, R′=Me 53%
**c**, R=H, R′=$CH_2$=$CHCH_2$ 47%
**d**, R=H, R′=$Me_2C$=$CHCH_2$ 48%

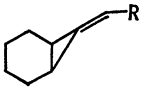
*Alkylidenecyclopropane Synthesis.* The 1-alkyl-1-bromocyclopropanes **3a**—**c**, **5a** and **5c** were easily

transformed into alkylidenecyclopropanes **15a—c** and **16a, b** in good yields by means of potassium *t*-butoxide in dimethyl sulfoxide. The rather mild reaction conditions prevent the subsequent thermal isomerization of the products. Consequently the alkylation of carbenoids **7** and **8** followed by dehydrobromination provides a variety of alkylidenecyclopropanes[15] which are otherwise difficultly accessible.



**15**

**a**, R=Ph 87%
**b**, R=*n*-$C_6H_{13}$ 62%
**c**, R=$PhCH_2OCH_2$ 68%



**16**

**a**, R=H 48%
**b**, R=$CH_2$=CH 66%

*Stereochemistry of 3, 4, 5 and 6.* The configurational assignment of monoalkylated products was based on PMR spectra (see the Experimental). Methyl substituent *cis* to phenyl group on cyclopropane ring (*e.g.* **3a**, $\delta$ 1.43) appeared at higher field than its *trans* isomer (**4a**, $\delta$ 1.93).[16] This applies to other isomers **3d**, **4d**; **3f**, **4f**. The bridge head protons of **5a** *cis* to halogen atom and *trans* to alkyl group on cyclopropane ring appeared at lower field than that of its isomer **6a**. The latter criterion is principally based on the deshielding effect[17] of the *trans* alkyl group and of the vicinal bromine atom as well. This assignment is also ascertained by the reactivity of each isomer under solvolytic conditions. Thus, 7-*exo*-bromo isomer **5a** was solvolyzed into **12a**, while the isomer **6a** was susceptible to ring opening.

## Experimental

All the temperatures are uncorrected. The IR spectra were obtained on a Shimadzu spectrometer 27-G, MS on a Hitachi RMU-6L, and PMR on JEOL JNM-PMX 60, Varian EM-360, or Varian HA-100D spectrometers. Butyllithium was purchased from Aldrich Co., Ltd. Commercial copper(I) iodide was purified according to the literature.[18] Copper(I) phenylacetylide was prepared by the Castro's method[19] and vacuum dried before use. Tetrahydrofuran (THF) was dried on lithium aluminum hydride and freshly distilled before use. HMPA was dried on calcium hydride and distilled. The cold bath of −95 °C was prepared by mixing liquid nitrogen and toluene (freezing point of toluene). All the reactions were carried out under a nitrogen atmosphere.

*gem-Dihalocyclopropanes.* Dibromocarbene adducts were prepared by the reaction of bromoform and *t*-BuOK with the corresponding olefins. 1,1-Dichloro-2-phenylcyclopropane was obtained by the phase transfer method ($CHCl_3$/NaOH, hexadecyltrimethylammonium bromide). A typical procedure is given for the synthesis of **1c**.

*1,1-Dibromo-2-(benzyloxymethyl)cyclopropane (1c).* A suspension of *t*-BuOK (60 g, 0.45 mol, containing 26% of *t*-BuOH) in dry hexane (100 ml) was cooled to 0 °C and mixed with benzyl allyl ether (43 g, 0.36 mol). A solution of $CHBr_3$ (91 g, 0.36 mol) in hexane (50 ml) was added at such a rate as to maintain the temp. below 10 °C (*ca.* 2 h). After the addition was complete, stirring was continued for 14 h at room temp. The reaction mixture was then treated with water (100 ml) and extracted with four 200 ml portions of hexane. The combined organic layer was washed with three 100 ml portions of brine, dried ($Na_2SO_4$) and concentrated. The oily residue was fractionated through a 15 cm Vigreux column under reduced pressure. The product **1c** was collected at 120—129 °C/0.28 mmHg (18 g, 20% yield). Analytically pure sample was obtained by preparative TLC (silica gel, hexane–ether 10: 1, $R_f$ 0.6—0.7). IR (neat): 3090, 3060, 3030, 2850, 1495, 1455, 1366, 1108, 730, 691, 676 $cm^{-1}$; MS: *m/e* (%), 322 ($M^+$+4, 0.08), 320 ($M^+$+2, 0.16), 318 ($M^+$, 0.08), 91 (100); PMR ($CCl_4$): $\delta$ 1.1—2.1 (m, 3H), 3.50 (d, $J$=6 Hz, 2H, $OC\underline{H}_2C$), 4.46 (s, 2H, $PhC\underline{H}_2$), 7.1—7.5 (m, 5H, Ph). Found: C, 41.5; H, 3.7%. Calcd for $C_{11}H_{12}Br_2O$: C, 41.3; H, 3.8%.

*1-Bromo-1-methyl-2-phenylcyclopropanes (3a and 4a).* The procedure exemplifies the preparation and alkylation of α-halocyclopropyllithiums.

*Conditions A.* A magnetically stirred solution containing 1.4 g (5.0 mmol) of **1a** in 10 ml of THF was cooled to −95 °C and maintained approximately at this temp. during the addition (5 min) of a solution of *n*-BuLi in hexane (4.3 ml of 1.17 M solution, 5.0 mmol). The reaction mixture was stirred at −95 °C for 10 min, treated with MeI (1.0 ml, *ca.* 3 eq) over 5 min, allowed to warm to room temp. in 2 h and quenched with water. Workup and distillation at 70—80 °C/4 mmHg of the oily residue gave 0.74 g (70% yield) of *r*-1-bromo-1-methyl-*t*-2-phenylcyclopropane (**3a**): bp 70—71 °C/4 mmHg; IR (neat): 1608, 1583, 1500, 1451, 1387, 1157, 1090, 770, 735, 700, 605 $cm^{-1}$; MS: *m/e* (%), 212 ($M^+$+2, 2), 210 ($M^+$, 2), 131 (100), 117 (8), 91 (42); PMR ($CCl_4$): $\delta$ 1.17 (t, $J$=7 Hz, 1H), 1.43 (s, 3H, Me), 1.55 (dd, $J$=7, 10 Hz, 1H), 2.74 (dd, $J$=7, 10 Hz, 1H, $PhC\underline{H}$), 6.8—7.5 (m, 5H, Ph). Found: C, 56.9; H, 5.4%. Calcd for $C_{10}H_{11}Br$: C, 56.9; H, 5.3%.

*Conditions B.* A magnetically stirred solution containing 0.28 g (1.0 mmol) of **1a** and 0.5 ml of MeI in 5 ml of THF was cooled to −95 °C and maintained approximately at this temp. during the addition of *n*-BuLi (1.1 mmol, 1.00 M in hexane) over a 5 min period. Stirring was continued at −95 °C for 30 min and the temp. was raised gradually to room temp. in 2 h. After aqueous workup short-path distillation at 72—82 °C/4 mmHg gave an isomeric mixture of 1-bromo-1-methyl-2-phenylcyclopropanes (see Table 1). Each isomer was separated by preparative GLC on a 1 m stainless steel column packed with 20% Silicone HV grease coated Celite 545 (column temp 150 °C; carrier gas, He; 1.0 kg/$cm^2$; $R_t$ 20 min for *trans* isomer and 21 min for *cis* one).

r-*1-Bromo-1-methyl-c-2-phenylcyclopropane (4a)*: bp 58—61 °C/3 mmHg; IR (neat): 1605, 1582, 1499, 1450, 1260, 1167, 760, 730, 695 $cm^{-1}$; MS: *m/e* (%), 212 ($M^+$+2, 2), 210 ($M^+$, 2), 131 (100), 117 (21), 91 (41); PMR ($CCl_4$): $\delta$ 1.25 (dd, $J$=7, 10 Hz, 1H), 1.50 (t, $J$=7 Hz, 1H), 1.93 (s, 3H, Me), 1.96 (dd, $J$=7, 10 Hz, 1H, $PhC\underline{H}$), 7.0—7.4 (m, 5H, Ph). Found: C, 56.7; H, 5.3%. Calcd for $C_{10}H_{11}Br$: C, 56.9; H, 5.3%.

*Conditions C.* A magnetically stirred solution containing 0.28 g (1.0 mmol) of **1a**, 1 ml of HMPA, and 0.5 ml of MeI in THF (10 ml) was cooled to −95 °C. The same operation as the conditions B, followed by short-path distillation at 70—80 °C/4 mmHg, gave a mixture of **3a** and **4a** (Table 1).

r-*1-Bromo-1-methyl-t-2-hexylcyclopropane (3b)*: bp 50—51 °C/3 mmHg; IR (neat): 3080, 1470, 1380, 1154, 1032, 729 $cm^{-1}$; MS: *m/e* (%), 220 ($M^+$ 2, 0,9), 218 ($M^+$, 0.9), 139 (3), 97 (25), 83 (58), 69 (61), 55 (100), 41 (100); PMR ($CCl_4$): $\delta$ 0.2—0.5 (m, 1H), 0.7—1.7 (m, 15H), 1.70 (s, 3H, Me). Found: C, 54.6; H, 8.9%. Calcd for $C_{10}H_{19}Br$: C, 54.8; H,

8.7%.

r-*1-Bromo-1-methyl*-c-*2-hexylcyclopropane* (**4b**): bp 55—65 °C (bath temp)/3 mmHg; IR (neat): 3060, 1440, 1369, 1165, 1020 $cm^{-1}$; MS: *m/e* (%), 220 ($M^+$+2, 0.9), 218 ($M^+$, 0.9), 139 (3), 97 (28), 83 (63), 69 (65), 55 (98), 41 (100); PMR ($CCl_4$): δ 0.6—0.8 (m, 2H), 0.8—1.7 (m, 14H), 1.73 (s, 3H, Me). Found: C, 55.0; H, 8.7%. Calcd for $C_{10}H_{19}Br$: C, 54.8; H, 8.7%.

r-*1-Bromo-1-methyl*-t-*2-(benzyloxymethyl)cyclopropane* (**3c**): bp 87—93 °C (bath temp)/0.1 mmHg; IR (neat): 3080, 3050, 1605, 1585, 1496, 1451, 1375, 1165, 1145, 1095, 1025, 733, 695 $cm^{-1}$; MS: *m/e* (%), 256 ($M^+$+2, 0.07), 254 ($M^+$, 0.07), 145 (7), 105 (5), 91 (100), 77 (5); PMR ($CCl_4$): δ 0.58 (t, $J$= 6 Hz, 1H), 1.0—1.5 (m, 2H), 1.72 (s, 3H, Me), 3.1—3.7 (m, 2H, $OCH_2$), 4.43 (s, 2H, PhC$\underline{H}_2$), 7.1—7.5 (m, 5H, Ph). Found: C, 56.4; H, 5.9%. Calcd for $C_{12}H_{15}BrO$: C, 56.5; H, 5.9%.

r-*1-Bromo-1-methyl*-c-*2-(benzyloxymethyl)cyclopropane* (**4c**): bp 95—105 °C (bath temp)/0.06 mmHg; IR (neat): 3030, 1494, 1451, 1370, 1168, 1090, 1026, 739, 700 $cm^{-1}$; MS: *m/e* (%), 256 ($M^+$+2, 0.1), 254 ($M^+$, 0.1), 91 (100); PMR ($CCl_4$): δ 0.8—1.4 (m, 3H), 1.77 (s, 3H, Me), 3.2—3.8 (m, 2H, $OCH_2$), 4.49 (s, 2H, PhC$\underline{H}_2$), 7.1—7.6 (m, 5H, Ph). Found: C, 56.4; H, 6.0%. Calcd for $C_{12}H_{15}BrO$: C, 56.5; H, 5.9%.

r-*1-Chloro-1-methyl*-t-*2-phenylcyclopropane* (**3f**): bp 40—50 °C (bath temp)/3 mmHg, IR (neat): 3040, 1604, 1500, 1450, 1382, 1165, 1090, 779, 703 $cm^{-1}$; MS: *m/e* (%), 168 ($M^+$+2, 1), 166 ($M^+$, 3), 131 (100), 115 (19), 103 (5), 91 (38); PMR ($CCl_4$): δ 1.0—1.7 (m, 2H), 1.30 (s, 3H, Me), 2.65 (dd, $J$=7, 10 Hz, 1H, PhC$\underline{H}$), 7.1—7.4 (m, 5H, Ph). Found: C, 71.8; H, 6.6%. Calcd for $C_{10}H_{11}Cl$: C, 72.1; H, 6.7%.

r-*1-Chloro-1-methyl*-c-*2-phenylcyclopropane* (**4f**): bp 55—65 °C (bath temp)/20 mmHg; IR (neat): 3040, 1600, 1500, 1450, 1170, 880, 764, 730, 700 $cm^{-1}$; MS: *m/e* (%), 168 ($M^+$+2, 1.4), 166 ($M^+$, 4.5), 131 (100), 115 (20), 103 (6), 91 (38); PMR ($CCl_4$): δ 1.1—1.6 (m, 2H), 1.77 (s, 3H, Me), 2.12 (dd, $J$=7, 10 Hz, 1H, PhC$\underline{H}$), 7.1—7.3 (m, 5H, Ph). Found: C, 72.0; H, 6.7%. Calcd for $C_{10}H_{11}Cl$: C, 72.1; H, 6.7%.

exo-*7-Bromo-7-methylnorcarane* (**5a**): bp 70—90 °C (bath temp)/22 mmHg; IR (neat): 3040, 1470, 1450, 1440, 1382, 1171, 1075, 832, 799, 750 $cm^{-1}$; MS: *m/e* (%), 190 ($M^+$+2, 3), 188 ($M^+$, 3), 146 (10), 109 (91), 67 (100); PMR ($CCl_4$): δ 1.70 (s, 3H, Me), 1.0—2.3 (m, 10H). Found: C, 50.8; H, 6.7%. Calcd for $C_8H_{13}Br$; C, 50.8; H, 6.9%.

endo-*7-Bromo-7-methylnorcarane* (**6a**): bp 50—55 °C (bath temp)/2 mmHg; IR (neat): 3000, 1463, 1445, 1382, 1247, 1175, 1105, 867, 810 $cm^{-1}$; MS: *m/e* (%), 190 ($M^+$+2, 4), 188 ($M^+$, 4), 146 (13), 109 (93), 67 (100); PMR ($CCl_4$): δ 1.76 (s, 3H, Me), 0.8—1.0 (m, 2H), 1.1—2.5 (m, 8H). Found: C, 51.0; H, 7.1%. Calcd for $C_8H_{13}Br$: C, 50.8; H, 6.9%.

exo-*7-Bromo-1,7-dimethylnorcarane* (**5b**): bp 42 °C/1 mmHg; IR (neat): 1447, 1375, 1229, 1069 $cm^{-1}$; MS: *m/e* (%), 204 ($M^+$+2, 3), 202 ($M^+$, 3), 187 (5), 146 (5), 123 (100), 81 (89), 67 (54); PMR ($CCl_4$): δ 0.8—2.3 (m, 9H), 1.40 (s, 3H, Me), 1.76 (s, 3H, Me). Found: C, 53.1; H, 7.3%. Calcd for $C_9H_{15}Br$: C, 53.2; H, 7.4%.

endo-*7-Bromo-1,7-dimethylnorcarane* (**6b**): bp 65—70 °C (bath temp)/16 mmHg; IR (neat): 1440, 1250, 1095, 787 $cm^{-1}$; MS: *m/e* (%), 204 ($M^+$+2, 3), 202 ($M^+$, 3), 187 (4), 146 (5), 123 (79), 81 (85), 67 (100); PMR ($CCl_4$): δ 0.5—0.7 (m, 1H), 1.15 (s, 3H, Me), 1.1—2.1 (m, 8H), 1.83 (s, 3H, Me). Found: C, 53.3; H, 7.5%. Calcd for $C_9H_{15}Br$: C, 53.2; H, 7.4%.

*1-Allyl-1-bromo-2-phenylcyclopropanes*. A solution of *n*-BuLi in hexane (1.7 ml of 1.17 M solution, 2.0 mmol) was added to a cooled (−95 °C) solution of **1a** (0.55 g, 2.0 mmol) in THF (10 ml) over a 5 min period. After 30 min copper(I) iodide (0.19 g, 1.0 mmol) was added and 30 min thereafter allyl bromide (0.26 g, 2.0 mmol) diluted with HMPA (1 ml) was added. Stirring for 4 h and subsequent workup gave a mixture of **3d** and **4d** (0.28 g, 59% yield, bp 85—95 °C/4 mmHg). Each isomer was separated by preparative GLC (Silicone HV grease, similar condition as described in conditions B).

*1-Allyl*-r-*1-bromo*-t-*2-phenylcyclopropane* (**3d**): bp 90—95 °C/4 mmHg; IR (neat): 1644, 1606, 1500, 1452, 1429, 1238, 1202, 1150, 918, 772, 738, 700 $cm^{-1}$; MS: *m/e* (%), 238 ($M^+$+2, 1), 236 ($M^+$, 1), 157 (48), 129 (52), 115 (95), 91 (100); PMR ($CCl_4$): δ 1.2—2.4 (m, 4H), 2.81 (dd, $J$=7, 10 Hz, 1H, PhC$\underline{H}$), 4.7—5.9 (m, 3H), 7.1—7.3 (m, 5H, Ph). Found: C, 60.5; H, 5.4%. Calcd for $C_{12}H_{13}Br$: C, 60.8; H, 5.5%.

*1-Allyl*-r-*1-bromo*-c-*2-phenylcyclopropane* (**4d**): bp 84—94 °C (bath temp)/4 mmHg; IR (neat): 1640, 1603, 1582, 1499, 1450, 1430, 1266, 1150, 1043, 998, 920, 764, 732, 698 $cm^{-1}$; MS: *m/e* (%), 238 ($M^+$+2, 1), 236 ($M^+$, 1), 157 (55), 129 (55), 115 (100), 91 (95); PMR ($CCl_4$): δ 1.2—1.6 (m, 2H), 2.01 (dd, $J$=7, 10 Hz, 1H, PhC$\underline{H}$), 2.2—3.0 (m, 2H), 4.9—6.3 (m, 3H), 6.8—7.3 (m, 5H, Ph). Found: C, 60.7; H, 5.5%. Calcd for $C_{12}H_{13}Br$: C, 60.8; H, 5.5%.

*1-Bromo-1-ethyl-2-phenylcyclopropanes* (**3e** *and* **4e**). A magnetically stirred suspension of copper(I) phenylacetylide (0.17 g, 1.0 mmol) in THF (5 ml) containing **1a** (0.28 g, 1.0 mmol) was cooled to −95 °C and the whole was maintained approximately at this temperature during the addition of *n*-BuLi in hexane (0.8 ml of 1.25 M solution, 1.0 mmol) over 5 min. Five min after the addition ethyl iodide (0.10 ml, *ca.* 1.2 mmol) and 15 min thereafter HMPA (1 ml) were added. The mixture was maintained at −95 °C for successive 5 h and warmed gradually to room temp (14 h). Workup and short-path distillation of the crude product at 60—80 °C/3 mmHg gave an isomeric mixture of **3e** and **4e** (0.12 g, 54% yield). Each isomer was separated by preparative GLC (Silicone HV grease, see conditions B).

r-*1-Bromo-1-ethyl*-t-*2-phenylcyclopropane* (**3e**): $R_t$ 23 min; bp 72—74 °C/4 mmHg; IR (neat): 1603, 1580, 1497, 1454, 1140, 804, 770, 733, 699 $cm^{-1}$; MS: *m/e* (%), 226 ($M^+$+2, 0.8), 224 ($M^+$, 0.8), 145 (100), 130 (14), 117 (31). 91 (32); PMR ($CCl_4$): δ 0.7—1.7 (m, 7H), 2.78 (dd, $J$=7, 10 Hz, 1H, PhC$\underline{H}$), 7.0—7.3 (m, 5H, Ph). Found: C, 58.6; H, 5.7%. Calcd for $C_{11}H_{13}Br$: C, 58.7; H, 5.8%.

r-*1-Bromo-1-ethyl*-c-*2-phenylcyclopropane* (**4e**): $R_t$ 25 min; bp 99—103 °C (bath temp)/4 mmHg; IR (neat): 1602, 1580, 1496, 1450, 1370, 1157, 1025, 824, 752, 730, 694 $cm^{-1}$; MS: *m/e* (%), 226 ($M^+$+2, 0.7), 224 ($M^+$, 0.7), 145 (100), 130 (14), 117 (50), 91 (42); PMR ($CCl_4$): δ 1.0—2.1 (m, 8H), 7.0—7.3 (m, 5H, Ph). Found: C, 58.6; H, 5.9%. Calcd for $C_{11}H_{13}Br$: C, 58.7; H, 5.8%.

endo-*7-Allyl-7-bromonorcarane* (**5c**). A suspension of copper(I) iodide (0.48 g, 2.5 mmol) in THF (15 ml) containing **2a** (1.3 g, 5.0 mmol) was cooled to −95 °C and a solution of *n*-BuLi in hexane (2.7 ml of 2.0 M solution, 5.5 mmol) was added to this suspension during the period of 5 min. After 10 min allyl bromide (1.0 ml) was added and stirring was continued for 4 h. The mixture was gradually warmed up to room temp in 2 h and quenched with water. Workup and extraction with ether followed by distillation at 80—90 °C/2 mmHg gave **5c** (0.94 g, 87% yield). Preparative GLC (Silicone HV grease, 120 °C, 1.0 kg/$cm^2$, $R_t$ 15 min) gave the analytically pure sample. Bp 77—80 °C/2 mmHg; IR (neat): 3090, 3010, 1643, 1470, 1452, 1426, 1224, 1168, 1115, 1049, 980, 910, 835 $cm^{-1}$; MS *m/e*: (%), 216 ($M^+$+2, 2), 214 ($M^+$, 2), 172 (2), 135 (77), 93 (78), 79 (66), 67 (100); PMR ($CCl_4$): δ 0.9—2.2 (m, 10H), 2.57 (dt, $J$=6.2, 1 Hz, 2H, $CH_2$=

$CHC\underline{H}_2$), 4.9—6.3 (m, 3H). Found: C, 55.8; H, 7.2%. Calcd for $C_{10}H_{15}Br$: C, 55.8; H, 7.0%.

exo-*7-Bromo-7-(3-methyl-2-butenyl)norcarane (5d)*. A magnetically stirred solution containing **2a** (0.51 g, 2.0 mmol) in THF (10 ml) was cooled to −95 °C and maintained at this temp during the dropwise addition of a solution of *n*-BuLi (1.0 ml of 2.1 M hexane solution, 2.2 mmol) over a 5 min period. The reaction mixture was stirred at −95 °C for 10 min and 3-methyl-2-butenyl bromide (0.35 g, 2.4 mmol) diluted with HMPA (1 ml) was added at −95 °C over 5 min. The reaction mixture was allowed to warm to −78 °C in 2 h and quenched with ethanol (1 ml). Workup and preparative TLC (silica gel, hexane, $R_f$ 0.7) gave pure **5d** (0.37 g, 77% yield). Bp 100—103 °C/4 mmHg; IR (neat): 3030, 1670, 1470, 1445, 1370, 1170, 1115, 1095, 1045, 805 $cm^{-1}$; MS: *m/e* (%), 244 ($M^+$+2, 0.9), 242 ($M^+$, 0.9), 227 (0.5), 199 (12), 186 (24), 163 (54), 107 (99), 41 (100); PMR ($CCl_4$): $\delta$ 0.9—2.3 (m, 16H), 2.47 (d, $J$=6 Hz, 2H), 5.0—5.5 (m, 1H). Found: C, 59.1; H, 8.0%. Calcd for $C_{12}H_{19}Br$: C, 59.3; H, 7.9%.

trans-*1-Bromo-2-phenylcyclopropane (3g)*.[12a] According to the procedure of conditions A the carbenoids were generated and quenched with ethanol (2 ml) instead of MeI, and the reaction mixture was warmed up to room temp. Workup and distillation at 109—113 °C/19 mmHg gave 87% yield of **3g**. IR (neat): 3030, 1600, 1498, 1229, 758, 700, 620 $cm^{-1}$; MS: *m/e* (%), 198 ($M^+$+2, 0.5), 196 ($M^+$, 0.5), 195 (0.5), 117 (100), 115 (47), 91 (23); PMR: ($CCl_4$) $\delta$ 1.2—1.6 (m, 2H), 2.1—2.5 (m, 1H), 2.7—3.1 (m, 1H), 6.7—7.5 (m, 5H, Ph).

trans-*1-Bromo-2-hexylcyclopropane (3h)*[12g] *with Concomitant 4h (19%)*: Bp 77—80 °C/19 mmHg; IR (neat): 3060, 1470, 1375, 1236, 1034, 920 $cm^{-1}$; MS: *m/e* (%), 206 ($M^+$+2, 0.3), 204 ($M^+$, 0.3), 162 (2), 148 (4), 83 (49), 69 (100), 55 (88); PMR ($CCl_4$): $\delta$ 0.6—1.8 (m, 16H), 2.4—2.7 (m, 1H, CHBr).

trans-*2-(Benzyloxymethyl)-1-bromocyclopropane (3i)*: Bp 90—98 °C (bath temp)/0.07 mmHg; IR (neat): 3040, 1600, 1493, 1450, 1090, 740, 700 $cm^{-1}$; MS: *m/e* (%), 242 ($M^+$+2, 0.9), 240 ($M^+$, 0.9), 210 (0.8), 161 (1.5), 131 (11), 91 (100); PMR ($CCl_4$): $\delta$ 0.8—1.8 (m, 3H), 2.5—2.9 (m, 1H, CHBr), 3.1—3.6 (m, 2H, $OCH_2$), 4.42 (s, 2H, $PhC\underline{H}_2$), 7.1—7.4 (m, 5H, Ph). Found: C, 55.1; H, 5.3%. Calcd for $C_{11}H_{13}BrO$: C, 54.8; H, 5.4%.

trans-*1-Chloro-2-phenylcyclopropane (3j)*:[20] bp 90—100 °C (bath temp)/19 mmHg; IR (neat): 3040, 1605, 1499, 1450, 1253, 940, 888, 760, 700, 680 $cm^{-1}$; MS: *m/e* (%), 154 ($M^+$+2, 3), 152 ($M^+$, 8), 117 (100), 115 (43), 91 (18); PMR ($CCl_4$): $\delta$ 1.2—1.6 (m, 2H), 2.1—2.5 (m, 1H), 2.9—3.3 (m, 1H, CHCl), 6.9—7.5 (m, 5H, Ph).

cis-*1-Chloro-2-phenylcyclopropane (4j)*:[20] Bp 89—95 °C (bath temp)/19 mmHg; IR (neat): 3030, 1600, 1495, 1450, 1278, 1078, 917, 812, 767, 730, 700, 658, 591 $cm^{-1}$; MS: *m/e* (%), 154 ($M^+$+2, 3), 152 ($M^+$, 8), 117 (100), 115 (46), 91 (9); PMR ($CCl_4$): $\delta$ 1.0—1.6 (m, 2H), 2.0—2.5 (m, 1H), 3.1—3.4 (m, 1H, CHCl), 7.0—7.5 (m, 5H, Ph).

exo-*7-Bromonorcarane (5e)*:[12a] Bp 63—68 °C (bath temp)/18 mmHg; IR (neat): 3010 1448 1330 1215 1006 760 685 $cm^{-1}$; MS: *m/e* (%) 176 ($M^+$+2, 7) 174 ($M^+$, 7) 132 (16) 95 (100), 67 (54); PMR ($CCl_4$): $\delta$ 0.7—2.3 (m, 10H), 2.50 (t, $J$=3.5 Hz, CHBr).

exo-*7-Bromo-1-methylnorcarane (5f)*:[21] Bp 55—59 °C (bath temp)/1 mmHg; IR (neat): 1450, 1375, 1231, 700 $cm^{-1}$; MS: *m/e* (%), 190 ($M^+$+2, 0.4), 188 ($M^+$, 0.4), 173 (0.8), 109 (100), 93 (12), 81 (24), 67 (96), 55 (36); PMR ($CCl_4$): $\delta$ 0.8—2.2 (m, 9H), 1.25 (s, 3H, Me), 2.70 (d, $J$=4 Hz, CHBr). (Found: C, 51.1; H, 7.1%).

*(E)-β-Methylcinnamyl Acetate (9a)*. A suspension of silver acetate (87 mg, 0.52 mmol) and silver tetrafluoroborate (15 mg, 0.07 mmol) in a solution of **3a** (0.11 g, 0.52 mmol) and acetic acid (1.0 ml) was stirred at 75 °C for 22 h. Workup, followed by preparative TLC (silica gel, benzene, $R_f$ 0.6), gave **9a** (74 mg, 74% yield). Bp 70—77 °C (bath temp)/3 mmHg; IR (neat): 3080, 3050, 1740, 1660, 1600, 1580, 1493, 1445, 1370, 1230, 1120, 745, 700 $cm^{-1}$; MS: *m/e* (%), 190 ($M^+$, 21), 148 (37), 130 (74), 115 (59), 77 (13), 43 (100); PMR ($CCl_4$): $\delta$ 1.87 (s, 3H, Me), 2.04 (s, 3H, OAc), 4.57 (s, 2H, $CH_2O$), 6.47 (s, 1H, $PhC\underline{H}$), 7.1—7.4 (m, 5H, Ph). Found: C, 75.6; H, 7.5%. Calcd for $C_{12}H_{14}O_2$: C, 75.8; H, 7.4%.

*Solvolysis of 3b*. A mixture of **9b** and **10b** was obtained and each isomer was separated by preparative GLC (Silicone HV grease, 130 °C, 1.0 kg/$cm^2$).

*(E)-2-Methyl-2-nonen-1-yl Acetate (9b)*: $R_t$ 10 min; bp 64—72 °C (bath temp)/3 mmHg; IR (neat): 1736, 1464, 1370, 1225, 1015 $cm^{-1}$; MS: *m/e* (%), 198 ($M^+$, 0.3), 156 (6), 138 (14), 95 (23), 68 (41), 43 (100),; PMR ($CCl_4$): $\delta$ 0.7—1.5 (m, 13H), 1.63 (s, 3H, Me), 1.98 (s, 3H, OAc), 4.37 (s, 2H), 5.42 (t, $J$=7 Hz, 1H). Found: C, 72.8; H, 11.4%. Calcd for $C_{12}H_{22}O_2$: C, 72.7; H, 11.2%.

*2-Methyl-1-nonen-3-yl acetate (10b)*: $R_t$ 8 min; bp 53—64 °C (bath temp)/1.5 mmHg; IR (neat): 3080, 1730, 1650, 1235, 1020, 900 $cm^{-1}$; MS: *m/e* (%), 156 ($M^+$−42, 8), 138 (8), 113 (8), 95 (16), 82 (15), 68 (25), 43 (100); PMR ($CCl_4$): $\delta$ 0.7—2.3 (m, 13H), 1.68 (s, 3H, Me), 1.95 (s, 3H, OAc), 4.7—5.2 (m, 3H); Found: C, 72.4; H, 11.1%. Calcd for $C_{12}H_{22}O_2$: C, 72.7; H, 11.2%.

*Solvolysis of 3c*. A mixture of 4-benzyloxy-2-methyl-2-buten-1-yl acetate (**9c**) and 1-benzyloxy-3-methyl-3-buten-2-yl acetate (**10c**) was obtained and separated by preparative TLC (silica gel, hexane–ether 5: 1).

**9c**: $R_f$ 0.3—0.4; bp 87—93 °C (bath temp)/1 mmHg; IR (neat): 3050, 3020, 1730, 1490, 1450, 1360, 1220, 1065, 1020, 737, 700 $cm^{-1}$; MS: *m/e* (%), 174 ($M^+$−60, 3), 159 (3), 105 (11), 91 (100), 43 (72); PMR ($CCl_4$): $\delta$ 1.63 (s, 3H, Me), 2.00 (s, 3H, OAc), 4.00 (d, $J$=6.5 Hz, 2H), 4.41 (s, 4H), 5.4—5.9 (m, 1H), 7.0—7.5 (m, 5H). Found: C, 72.0; H, 7.7%. Calcd for $C_{14}H_{18}O_3$: C, 71.8; H, 7.7%. The geometry of double bond is assumed to be (E) on the analogy of the solvolysis of **3a** to **9a**.

**10c**: $R_f$ 0.4—0.5; bp 85—95 °C (bath temp)/1 mmHg; IR (neat): 3030, 1732, 1650, 1494, 1450, 1362, 1230, 1095, 1025, 905, 740, 700 $cm^{-1}$; MS: *m/e* (%), 234 ($M^+$, 0.01), 174 (2), 91 (78), 65 (43), 43 (100); PMR ($CCl_4$): $\delta$ 1.73 (s, 3H, Me), 2.00 (s, 3H, OAc), 3.45 (d, $J$=6 Hz, 2H), 4.45 (s, 2H), 4.8—5.1 (m, 2H), 5.31 (t, $J$=6 Hz, 1H), 7.0—7.5 (m, 5H, Ph). Found: C, 72.0; H, 8.0%. Calcd for $C_{14}H_{18}O_3$: C, 71.8; H, 7.7%.

*Hydrolysis of 9b*. One drop of sodium methoxide in methanol (1 M) was added to a solution of **9b** (7.5 mg, 0.04 mmol) in $CH_2Cl_2$ (1 ml). After stirring at room temp for 1 h the reaction mixture was worked up. Preparative TLC (silica gel, hexane–ether (2: 1. $R_f$ 0.4—0.5) afforded *(E)*-2-methyl-2-nonen-1-ol (5.4 mg, quantitative yield). Bp 93—100 °C (bath temp)/20 mmHg; IR (neat): 3360, 1640, 1480, 1380, 1265, 1010 $cm^{-1}$; MS: *m/e* (%), 156 ($M^+$, 6), 138 (4), 109 (4), 95 (9), 83 (12), 71 (46), 55 (27), 40 (100); PMR ($CCl_4$): $\delta$ 0.6—2.2 (m, 14H), 1.63 (s, 3H, Me), 3.88 (s, 2H, $CH_2O$), 5.2—5.5 (m, 1H). The methyl signal of this alcohol is strictly different from that of (*Z*) isomer ($\delta$ 1.71).[22]

*Hydrolysis of 9a*. This reaction afforded (*E*)-β-methylcinnamyl alcohol in 65% yield. Bp 88—95 °C (bath temp)/3 mmHg; IR (neat): 3300, 3070, 3050, 3020, 1664, 1600, 1575, 1493, 1443, 1074, 1008, 739, 695 $cm^{-1}$; MS: *m/e* (%), 148 ($M^+$, 51), 133 (28), 115 (49), 105 (46), 91 (100); PMR ($CCl_4$): $\delta$ 1.84 (br s, 4H, Me and OH), 4.08 (br s, 2H, $CH_2O$),

6.4—6.6 (m, 1H), 7.0—7.5 (m, 5H, Ph). The product was identical in all respects with the authentic sample prepared from lithium aluminum hydride reduction of (*E*)-β-methylcinnamaldehyde.[23]

exo-*7-Acetoxy-7-methylnorcarane (**12a**)*. A solution of **5a** (0.15 g, 0.80 mmol) in acetic acid (1 ml) was added to a suspension of silver acetate (0.13 g, 0.80 mmol) and silver tetrafluoroborate (16 mg, 0.08 mmol) in acetic acid (2 ml). After stirring for 2 h at 75 °C the reaction mixture was neutralized by the addition of saturated sodium hydrogencarbonate aq solution and extracted with ether. The organic layer was dried over sodium sulfate and evaporated *in vacuo*. The crude product was purified by preparative TLC (silica gel, hexane–ether 4: 1, $R_f$ 0.5). **12a** was obtained in 63% yield (85 mg). Bp 62—72 °C (bath temp)/4 mmHg; IR (neat): 3050, 1745, 1450, 1370, 1240, 1189, 1113, 1020, 893 $cm^{-1}$; MS: *m/e* (%), 126 ($M^+$—42, 13), 111 (15), 44 (85), 43 (100); PMR ($CCl_4$): δ 0.9—2.2 (m, 10H), 1.38 (s, 3H, Me), 1.85 (s, 3H, OAc). Found: C, 71.2; H, 9.9%. Calcd for $C_{10}H_{16}O_2$: C, 71.4; H, 9.6%.

exo-*7-Acetoxy-7-allylnorcarane (**12c**)*: Bp 72—82 °C (bath temp)/3 mmHg; IR (neat): 3070, 3000, 1735,1637, 1449, 1361, 1220, 1175, 910, 790 $cm^{-1}$; MS: *m/e* (%), 194 ($M^+$, 0.2), 153 (14), 111 (17), 67 (23), 43 (100), 41 (41); PMR ($CCl_4$): δ 0.6—2.4 (m, 10H), 1.85 (s, 3H, Me), 2.57 (d, $J$= 6 Hz, 2H), 4.9—6.2 (m, 3H). Found: C, 73.9; H, 9.4%. Calcd for $C_{12}H_{18}O_2$: C, 74.2; H, 9.3%.

exo-*7-Acetoxy-7-(3-methyl-2-butenyl)norcarane (**12d**)*: Bp 66—76 °C (bath temp)/2 mmHg; IR (neat): 3000, 1735, 1460, 1445, 1360, 1230, 1063, 1048 $cm^{-1}$; MS: *m/e* (%), 222 ($M^+$, 0.1), 180 (10), 162 (21), 147 (62), 43 (100); PMR ($CCl_4$): δ 0.5—2.3 (m, 12H), 0.83 (s, 6H, $Me_2C$), 1.98 (s, 3H, OAc), 4.67 (t, $J$=7 Hz, 1H). Found: C, 75.7; H 10.1%. Calcd for $C_{14}H_{22}O_2$: C, 75.6; H, 10.0%.

exo-*7-Acetoxy-1,7-dimethylnorcarane (**12b**)*: Bp 61—69 °C (bath temp)/4 mmHg; IR (neat): 1740, 1445, 1369, 1250, 1232, 1190, 1120, 1020, 790 $cm^{-1}$; MS: *m/e* (%), 182 ($M^+$, 0.2), 167 (0.3), 140 (12), 125 (26), 95 (10), 43 (100); PMR ($CCl_4$): δ 0.5—0.8 (m, 1H), 0.9—2.2 (m, 8H), 1.07 (s, 3H, Me), 1.38 (s, 3H, Me), 1.90 (s, 3H, OAc). Found: C, 72.2; H, 10.1%. Calcd for $C_{11}H_{18}O_2$: C, 72.5; H, 10.0%.

*Acetolysis of a Mixture of **5a** and **6a**.* A mixture of **5a** and **6a** (36: 64) (0.19 g, 1.0 mmol) dissolved in acetic acid (1 ml) was treated with silver salts as above affording an inseparable mixture of **12a** and 2-methyl-2-cyclohepten-1-yl acetate (93 mg, **12a**/ring opened isomer 59: 41) in 55% yield. The ratio was estimated by its PMR (δ 1.37 (s, Me), 1.85 (s, OAc) for **12a**; δ 1.98 (s, AOc), 5.2—5.8 (m, CHOAc and olefinic proton) for its isomer).

*2-Phenyl-1-methylenecyclopropane (**15a**).*[24] A solution of **3a** (50 mg, 0.24 mmol) in dimethyl sulfoxide (0.5 ml) was added to a solution of *t*-BuOK (42 mg, containing 26% of *t*-BuOH, 0.30 mmol) in DMSO (3 ml) at room temp. After stirring for 1 h the reaction mixture was quenched with water and extracted with pentane. The yield was estimated by GLC (Silicone SE-30, indane as an internal standard). The pure sample was obtained by short-path distillation (50—58 °C/10 mmHg). IR (neat): 3080, 1745, 1603, 1496, 1452, 1198, 1118, 1014, 890, 743, 695 $cm^{-1}$; MS: *m/e* (%), 130 ($M^+$, 70), 129 (100), 128 (60), 115 (66); PMR ($CCl_4$): δ 1.0—1.9 (m, 2H), 2.4—2.8 (m, 1H), 5.5—5.8 (m, 2H), 7.0—7.5 (m, 5H, Ph).

*2-Hexyl-1-methylenecyclopropane (**15b**)*:[24] Bp 53—63 °C (bath temp)/20 mmHg; IR (neat): 3060, 3040, 1740, 1460, 1016, 885 $cm^{-1}$; MS: *m/e* (%), 138 ($M^+$, 3), 123 (16), 109 (18), 95 (37), 81 (100), 67 (88), 55 (80), 41 (70); PMR ($CCl_4$): δ 0.6—2.0 (m, 16H), 5.2—5.6 (m, 2H).

*2-(Benzyloxymethyl)-1-methylenecyclopropane (**15c**)*: Bp 65—75 °C (bath temp)/3 mmHg; IR (neat): 3060, 3040, 1735, 1600, 1580, 1492, 1450, 1350, 1080, 1021, 885, 735, 700 $cm^{-1}$; MS: *m/e* (%), 174 ($M^+$, 0.05), 129 (4), 107 (6), 91 (100), 65 (10); PMR ($CCl_4$): δ 0.7—2.0 (m, 3H), 3.0—3.6 (m, 2H), 4.45 (s, 2H), 5.3—5.6 (m, 2H), 7.1—7.5 (m, 5H). Found: C, 82.6; H, 8.3%. Calcd for $C_{12}H_{14}O$: C, 82.7; H, 8.1%.

*7-Methylenenorcarane (**16a**)*:[15f] Bp 65—75 °C (bath temp)/130 mmHg; IR (neat): 3060, 2970, 2700, 1749, 1452, 1351, 1331, 1140, 882, 848, 710 $cm^{-1}$; MS: *m/e* (%), 108 ($M^+$, 15), 107 (25), 93 (77), 91 (83), 79 (100), 55 (56); PMR ($CCl_4$): δ 0.8—2.1 (m, 10H), 5.2—5.4 (m, 2H).

*7-Allylidenenorcarane (**16b**)*: Bp 66—70 °C (bath temp)/4 mmHg; IR (neat): 3100, 2680, 1790, 1612. 1450 990 890 $cm^{-1}$; MS: *m/e* (%), 134 ($M^+$, 14), 119 (34), 105 (48), 91 (100), 80 (45), 79 (51), 77 (46), 67 (24); PMR ($CCl_4$): δ 1.1—2.5 (m, 10H), 4.8—5.5 (m, 2H), 6.0—6.9 (m, 2H). Exact mass : *m/e* 134.112 ($M^+$). Calcd for $C_{10}H_{14}$: *m/e* 134.110.

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