Stereoselective One-pot Dialkylation of *gem*-Dihalocyclopropanes by Means of Dialkylcopperlithiums

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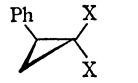
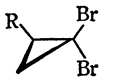
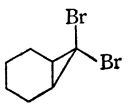
The transformation of *gem*-dihalocyclopropanes (**1**) into 1-alkyl-1-butylcyclopropanes (**2** and **3**) is established by successive treatment with dibutylcopperlithium and several electrophiles. This sequence is found to be stereochemically controllable and is successfully applied to *dl*-sirenin synthesis. In contrast to the reaction of dibutylcopperlithium, dimethyl- and divinylcopperlithiums convert 1,1-dibromo-2-phenylcyclopropane (**1a**) into 1-bromo-1-methyl- and 1-bromo-1-vinyl-2-phenylcyclopropanes (**15a**, **16a** and **15b**, **16b**) respectively.

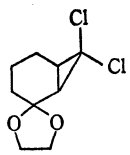
It is remarkable that a class of natural products commonly possess a substituted cyclopropane ring[1] in spite of the large strain energy therein involved. One of the most facile routes to the smallest carbocyclic ring is dihalocyclopropanation of olefins[2] by phase-transfer technique, but unfortunately efficient methodology has never been recorded for replacing each halogen atom of the dihalocarbene-adducts with two different alkyl groups successively. Although monoalkylation of *gem*-dihalocyclopropanes proceeds effectively and stereoselectively,[3] the second alkylation of the resulting α-alkylcyclopropyl halides has turned out extremely arduous. Remarkably, it is known that the reaction of *gem*-dihalides with dimethylcopperlithium results in *gem*-dimethylation.[4,5] Being interested in this particular observation we have carefully investigated the interaction of *gem*-dihalocyclopropanes with dibutylcopperlithium to find that α-butylcyclopropylcopper compounds thus initially produced react with methyl iodide giving stereoselectively the desired dialkylated products which have the methyl group always on the more hindered (*cis* or *endo*) site. On the basis of this finding a novel approach to sirenin synthesis has been exploited.[6]

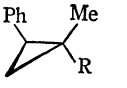
Reaction of gem-*Dihalocyclopropanes with Dibutylcopperlithium.* Upon treatment with 5 mol of dibutylcopperlithium the dibromocyclopropane **1a**, for example, produced a stereoisomeric mixture of organometallic species, which after workup with excess methyl

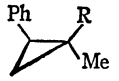

1a: X=Br
1b: X=Cl

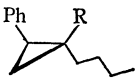

1c: R=*n*-C_6H_{13}
1d: R=$PhCH_2OCH_2$


1e


1f


2a: R=*n*-Bu
2b; R=*s*-Bu
2c: R=*t*-Bu


3a: R=*n*-Bu
3b: R=*s*-Bu
3c: R=*t*-Bu


2d: R=Et
2e: R=Ac
2f: R=H
2g: R=I

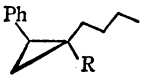
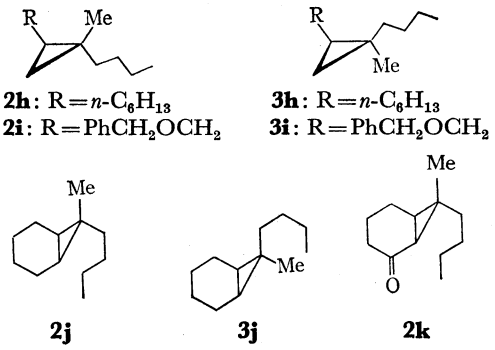

3d: R=Et
3e: R=Ac
3f: R=H
3g: R=I

Table 1. Stereoselective dialkylation of *gem*-dihalocyclopropanes

Entry	*gem*-Dihalocyclopropane	R^1[a]	R^2–Y[b]	Reaction temp (°C)	Products	Yield (%) of **2** and **3**	**2**:**3**
1	**1a**	*n*-Bu	MeI	−48	**2a** and **3a**	100	80:20
2	**1a**	*n*-Bu	MeI	−78	**2a** and **3a**	64	86:14
3	**1a**	*s*-Bu	MeI	−78	**2b** and **3b**	43	93:7
4	**1a**	*t*-Bu	MeI	−55	**2c**	20	100:0
5	**1a**	*n*-Bu	EtI	−48	**2d** and **3d**	65	51:49
6	**1a**	*n*-Bu	AcBr	−48	**2e** and **3e**	34	80:20
7	**1a**	*n*-Bu	HOEt	−48	**2f** and **3f**	96	81:19
8	**1a**	*n*-Bu	I_2	−48	**2g** and **3g**	79	66:34[c]
9	**1b**	*n*-Bu	MeI	−60	**2a** and **3a**	71	41:59[d]
10	**1c**	*n*-Bu	MeI	−48	**2h** and **3h**	50	76:24
11	**1d**	*n*-Bu	MeI	−48	**2i** and **3i**	50	70:30
12	**1e**	*n*-Bu	MeI	−48	**2j** and **3j**	82	99:1
13	**1f**	*n*-Bu	MeI	−48	**2k**[e]	78	100:0

a) Butyl group in dibutylcopperlithium. b) Electrophiles (see Scheme 1). c) 1,1-Dibutyl-2-phenylcyclopropane (**17c**) was obtained as a by-product (see Experimental). d) The reason for the inverted isomer-preference is not clear. e) After deacetalization of the primary product.

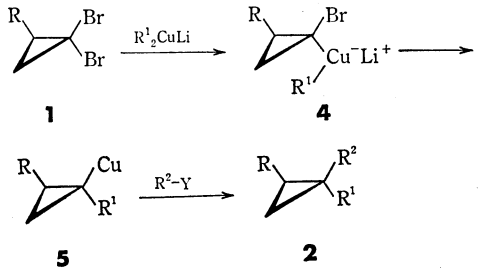


2h: R=*n*-C_6H_{13} **3h**: R=*n*-C_6H_{13}
2i: R=$PhCH_2OCH_2$ **3i**: R=$PhCH_2OCH_2$

2j **3j** **2k**

iodide afforded a 4: 1 mixture of **2a** and **3a** in a quantitative yield. Various *gem*-dihalocyclopropanes were allowed to react first with some dibutylcopperlithiums and then with a variety of electrophiles including methyl iodide. The results are summarized in Table 1. Preliminary experiments revealed, however, that the yields were very much influenced by the reaction conditions. Among solvent systems examined (hexane, hexane–ether, ether, tetrahydrofuran (THF), THF–hexamethylphosphoric triamide (HMPA)) hexane–ether gave the best results. The strict absence of unchanged butyllithium should be assured and therefore a slight excess of cuprous iodide was used for the preparation of the cuprate. Finally, the reaction temperature should be controlled carefully: the temperature during the reaction of the cuprate with dihalocyclopropanes being adjusted at −40 to −78 °C and the second alkylation at −20 °C.

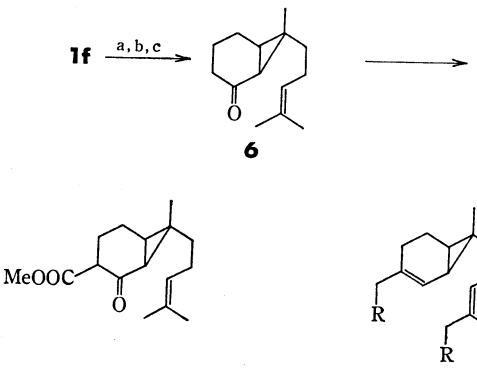
Of importance in the alkylation is the stereochemical consequence. The reaction of **1a** under the condition cited above resulted in the preferred formation of *cis*-methyl isomer (entry 1). The ratio was better at low temperatures, while the use of more polar solvent systems (THF or THF–HMPA) or the presence of *n*-Bu_3P as a ligand gave no improvement. Reaction of **1a** with di-*s*-butylcopperlithium or di-*t*-butylcopperlithium followed by methylation afforded predominantly *cis*-methylated **2b** and **2c** albeit in lower yields (entry 3, 4). Noteworthy is the reaction of 7,7-dibromonorcarane (**1e**) and its derivative **1f**, in which *endo*-methyl isomers (**2j** and **2k**) were formed exclusively (entry 12 and 13).



Scheme 1.

These stereochemical results are explained by Scheme 1 which involves halogen-copper exchange *at the less hindered halogen*, the consecutive S_N2 type alkyl migration (*inversion on the cyclopropane carbon*), and the second alkylation by R^2–Y with *retention of configuration*. The steric hindrance of large substituent(s) and/or the bulkiness of the copper reagent would strongly direct the dialkylcuprate to attack the less hindered halogen.

The configurational stability of α-alkylcyclopropylcopper reagent of type 5 was verified as follows. At −78 °C the dibromocyclopropane **1a** was treated with 5 mol of dibutylcopperlithium which had been prepared at −48 °C, and then the reaction mixture was gradually warmed up finally to −10 °C in *ca.* 3 h. Aliquots of the sample at various temperatures were withdrawn, quenched with methanol and the products, 1-butyl-2-phenylcyclopropanes (**2f** and **3f**), were analyzed by GLC to give a nearly invariable ratio of 4: 1 of **2f**/**3f** throughout the period of experiment. This indicates that the species **5** is configurationally stable at the temperature range examined.



a: $(Me_2C{=}CHCH_2CH_2)_2CuLi$; b: MeI; c: H_2SO_4–H_2O; d: NaH–$(MeO)_2CO$.

8a: R=H **8b**: R=OH

Application to dl-*Sirenin Synthesis.*[7] With these observations in hand we extended the reaction to the preparation of a key intermediate of *dl*-sesquicarene and *dl*-sirenin syntheses. As attempted preparation of the dibromocarbene adduct of cyclohexenone ethylene acetal failed to success, we were compelled to start with the dichlorocarbene adduct **1f** which was obtained by the phase-transfer technique.[2] Treatment of **1f** with bis-(4-methyl-3-pentenyl)copperlithium and then with excess methyl iodide, followed by deacetalization, afforded **6** in 44% yield. The GLC and PMR analyses showed no contamination of the stereoisomer. The configuration was established by the methoxycarbonyla-

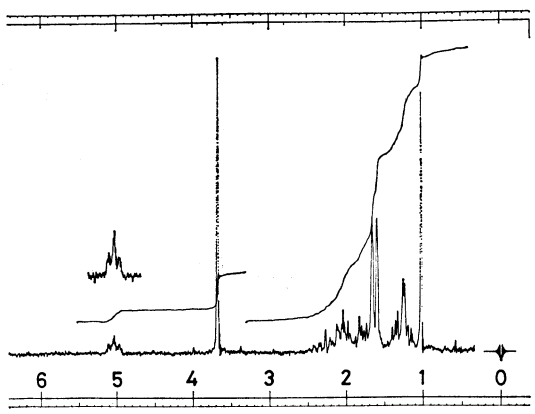
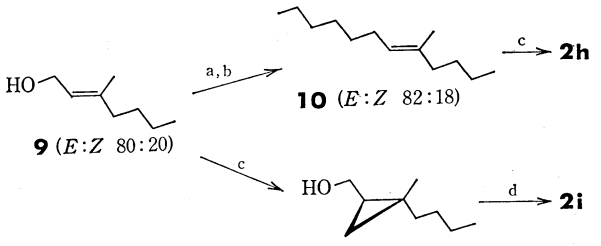


Fig. 1. The PMR spectrum of the keto ester **7** (CCl_4, 100 MHz).

tion of **6**. The methyl chemical shift (δ 1.02) of the product **7** (Fig. 1) was strictly the same as that of the 7-*endo*-methyl keto ester and clearly different from that of 7-*exo*-methyl isomer (δ 1.14).[7a] Further transformation of **7** to *dl*-sesquicarene (**8a**) and *dl*-sirenin (**8b**) has been already established.[7a]

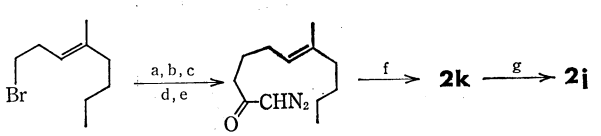
Stereochemistry of Dialkylated Cyclopropanes. The configuration of each phenyl substituted cyclopropane (**2a—g**, **3a—g**) was identified by the comparison of PMR spectra. In general, the methyl signal *cis* to phenyl group appeared at higher field than that of *trans* isomer (see Experimental).[3] For example, the methyl signal of **2a** appeared at δ 0.73, whereas that of its stereoisomer **3a** appeared at δ 1.18. Similarly, *cis*-acetylated cyclopropane **2e** showed acetyl signal at δ 1.61 and its *trans* isomer **3e** at δ 2.12. The peak shape analysis of butyl signal also afforded a basis for the stereochemical determination of **2d** and **2f**. The α-methylene proton peak of butyl group *cis* to phenyl group appeared at slightly higher field than that of the *trans* isomer due to the shielding effect of the benzene ring. The stereochemical assignment is also possible from the fact that proton(s) *cis* to butyl group on the three membered ring generally appeared at higher field than the *trans* proton(s) probably due to the deshielding effect by σ bond(s).[8] This criterion was applied to the determination of the iodinated cyclopropanes: benzylic proton of **2g** at δ 2.16 and that of **3g** at δ 2.78.



a: PBr_3; b: *n*-AmMgBr; c:CH_2I_2/Zn–Cu; d: NaH/$PhCH_2Cl$.

Scheme 2.

Stereochemistry of **2h** and **2i** was unambiguously determined by the independent syntheses as shown in Scheme 2. An allyl alcohol **9**[9] was converted into a trisubstituted olefin **10**, which was subjected to the Simmons-Smith reaction[10] to give **2h** and **3h** (84: 16). The authentic samples of **2i** and **3i** were obtained by cyclopropanation on **9** and the successive benzylation. Scheme 3 shows the syntheses of the authentic specimens of **2j** and **2k**. The route involves a well-established diazoketone cyclization.[11] Copper catalyzed thermal decomposition of **14** afforded **2k** and its stereoisomer (71: 29). The Wolff-Kishner reduction[12] of **2k** gave the hydrocarbon **2j**.

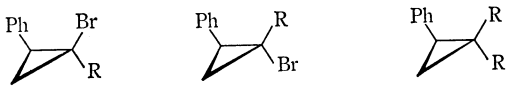


12 (*E*:*Z* 77:23) **14**

a: $NaCH(COOEt)_2$; b: NaOH; c: H_3O^+, Δ; d: $SOCl_2$; e: CH_2N_2; f: $CuSO_4$, Δ; g: NH_2NH_2, KOH, $HO(CH_2CH_2O)_3H$.

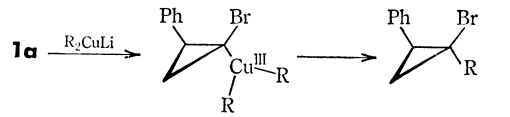
Scheme 3.

Further Extention and Possible Reaction Mcehanism. In sharp contrast to the above reaction of dibutylcuprates, dimethylcopperlithium reacted with **1a** in THF at —78 °C to afford dimethylated product **17a** (48%). Remarkably, the same procedure at —38 °C in ether gave a mixture (43: 57) of mono-methylated products **15a** and **16a** (49% yield) along with **17a** (17%). More drastic change of the reaction path was achieved only by temperature control in the reaction of divinylcopperlithium. Whereas at —48 °C in ether divinylcyclopropane **17b** was obtained in 47% yield, the reaction at —78 °C afforded 1-bromo-1-vinylcyclopropanes **15b** and **16b** (26: 74) in 80% yield. It should be noted that the reaction of **1a** with dibutylcopperlithium gave no **17c**.



15 **16** **17**

a: R=Me; **b**: R=vinyl; **c**: R=*n*-Bu

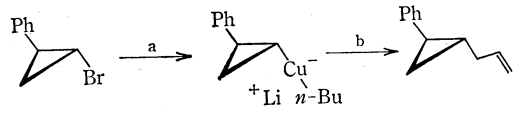


R=Me or vinyl **18** **15** or **16**

Scheme 4.

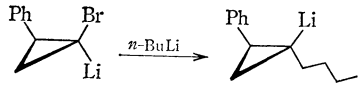
We do not believe that all these three cuprates react with **1a** by a single mechanism. The initial step in the reaction of dibutylcopperlithium shown in Scheme 1 is copper-halogen exchange (two-electron transfer process)[5a] to afford a mixed cuprate **4** which easily rearranges to an α-alkylated cyclopropylcopper **5** under S_N2 type alkyl migration. Another possibility is shown in Scheme 4 in which a trivalent copper species is assumed in the initial step. Reductive elimination of this unstable transient affords an α-alkylated cyclopro pyl bromide. The reaction of dimethyl- or divinylcopperlithium should be explained by this scheme, which is quite similar to the one proposed for the coupling of dialkylcuprates with alkyl halides and tosylates.[13]

The Scheme 1 is supported by the related observations as follows. When *trans*-1-bromo-2-phenylcyclopropane (**19**) was treated with 4 mol of dibutylcopperlithium in THF and successively with allyl bromide, *trans*-1-allyl-2-phenylcyclopropane (**20**) was obtained in 97% yield. No butylated product was detected and, therefore, the copper intermediate is probably the one as shown below. It should be noted that **19** was more susceptible to the reaction than its *cis* isomer.[14]



19 **20**

a: *n*-Bu_2CuLi/THF; b: CH_2=$CHCH_2Br$.



The second step in Scheme 1 is the intramolecular S_N2 type alkyl migration which is exemplified by the following experiment. A solution of **1a** in THF was added to a solution of butyllithium (3.3 mol) in THF at −95 °C. Aqueous workup afforded *trans*-1-butyl-2-phenylcyclopropane.[15] Introduction of butyl group is attributed to nucleophilic attack of butyl anion as illustrated below.[16]

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 and *t*-butyllithium were purchased from Aldrich Co. Ltd. Vinyllithium in ether,[17] methyllithium in ether,[18] and *s*-butyllithium in pentane[19] were prepared according to the literature. Commercial cuprous iodide was purified according to the literature.[20] Ether and hexane were distilled and dried on sodium metal. THF was dried on benzophenone ketyl and distilled. All the reactions were performed under a nitrogen atmosphere. The cold bath of −48 °C was prepared by mixing Dry Ice and *m*-xylene.

gem-*Dihalocyclopropanes.* These were prepared by the reaction of the corresponding olefins with bromoform/*t*-BuOK. *gem*-Dichlorocyclopropanes were prepared by the phase transfer method. A typical procedure is illustrated in the synthesis of **1f**.

*7,7-Dichloronorcaran-2-one Ethylene Acetal (**1f**).* A solution of cyclohexenone ethylene acetal (11.2 g, 80 mmol) in benzene (10 ml) was mixed with 120 ml of 50% aqueous sodium hydroxide. The mixture was warmed to 40 °C and under vigorous stirring 80 ml of chloroform was added during 4 h. After the addition was completed, the reaction mixture was stirred at 40 °C for 2 h. Extraction with hexane and subsequent fractionation through a 15 cm Vigreux column gave **1f** (88—90 °C/1 Torr, 11.6 g, 71% based on the consumed starting olefin). IR (neat): 1107, 1020, 948, 784 cm^{-1}; MS: *m/e* (%), 226 (M^++4, 0.5), 224 (M^+ +2, 2), 222 (M^+, 3.4), 187 (32), 99 (100), 86 (37); PMR (CCl_4): δ 1.0—2.3 (m, 8H), 3.7—4.2 (m, 4H). Found: C, 48.7; H, 5.7%. Calcd for $C_9H_{12}Cl_2O_2$: C, 48.5; H, 5.4%.

*1-Butyl-1-methyl-2-phenylcyclopropane (**2a** and **3a**).* Dibutylcopperlithium was prepared by the treatment of butyllithium (5.7 ml of 1.75 M hexane solution) with cuprous iodide (0.96 g, 5.0 mmol) suspended in ether (10 ml) at −48 °C. A solution of **1a** (0.28 g, 1.0 mmol) in ether (1 ml) was added dropwise to this solution. The reaction mixture was gradually warmed up to −20 °C in 1 h, treated with excess methyl iodide (1 ml), and further warmed to room temperature during 15 h. Workup followed by short path distillation at 82—92 °C/26 Torr gave a mixture of **2a** and **3a** (0.19 g, quantitative yield). Each isomer was separated by preparative GLC (20% Silicone HV grease on Celite 545, 1 m, 160 °C, He, 1.2 kg/cm^2).

r-*1-Butyl-1-methyl*-t-*2-phenylcyclopropane (**2a**)*: R_t 25 min; bp 84—89 °C (bath temp)/2 Torr; IR (neat): 3070, 3040, 1605, 1580, 1498, 1450, 1385, 1070, 1030, 780, 735, 700 cm^{-1}; MS: *m/e* (%), 188 (M^+, 16), 173 (2), 131 (100), 117 (15), 104 (32), 91 (34); PMR (CCl_4): δ 0.6—1.7 (m, 11H), 0.73 (s, 3H, Me), 1.83 (t, J=7 Hz, 1H, PhCH), 6.8—7.4 (m, 5H, Ph). Found: C, 89.3; H, 10.9%. Calcd for $C_{14}H_{20}$: C, 89.3; H, 10.7%.

r-*1-Butyl-1-methyl*-c-*2-phenylcyclopropane (**3a**)*: R_t 20 min; bp 85—95 °C (bath temp)/1 Torr; IR (neat): 3070, 3040, 1605, 1497, 1460, 1380, 1025, 777, 699 cm^{-1}: MS: *m/e* (%), 188 (M^+, 14), 173 (2), 131 (100), 117 (18), 104 (39), 91 (37); PMR (CCl_4): δ 0.5—1.6 (m, 11H), 1.18 (s, 3H, Me), 1.83 (dd, J=6, 8 Hz, 1H, PhC*H*), 6.9—7.4 (m, 5H, Ph). Found: C, 89.5; H, 10.7%. Calcd for $C_{14}H_{20}$: C, 89.3; H, 10.7%.

r-*1*-s-*Butyl-1-methyl*-t-*2-phenylcyclopropane (**2b**).* A cooled solution of *s*-butyllithium (16 ml of 0.62 M pentane solution, 10 mmol) was added to a suspension of cuprous iodide (0.95 g, 5.0 mmol) in ether (10 ml) at −78 °C. The suspension immediately turned to black, and after 5 min a solution of **1a** (0.28 g, 1.0 mmol) in ether (1 ml) was added. The reaction mixture was gradually warmed to −20 °C in 3 h, treated with methyl iodide (1 ml) and further warmed to room temp during the period of 5 h. Aqueous workup and subsequent preparative TLC (silica gel, hexane, R_f 0.7—0.8) afforded 83 mg of **2b** (93% pure on GLC assay). Analytical sample was obtained by preparative GLC. Bp 84—92 °C (bath temp)/23 Torr; IR (neat): 3060, 3040, 1603, 1575, 1498, 1450, 1370, 1075, 1020, 775, 733, 700 cm^{-1}: MS: *m/e* (%), 188 (M^+, 4), 131 (100), 117 (11), 104 (45); PMR (CCl_4): δ 0.3—1.7 (m, 11H), 0.61 (s, 3H, Me), 1.83 (dd, J=6, 8 Hz, 1H, PhC*H*), 6.7—7.3 (m, 5H, Ph). Found: C, 89.0; H, 10.6%. Calcd for $C_{14}H_{20}$: C, 89.3; H, 10.7%. GLC separation of minor components gave **3b** which was identified by MS: *m/e* 188 (M^+).

r-*1*-t-*Butyl-1-methyl*-t-*2-phenylcyclopropane (**2c**).* To di-*t*-butylcopperlithium, prepared from *t*-butyllithium (3.1 ml of 1.6 M pentane solution, 5.0 mmol) and cuprous iodide (0.48 g, 2.5 mmol) in ether (5 ml) at −55 °C, **1a** (0.14 g, 0.5 mmol) in ether (1 ml) was added, and the reaction mixture was gradually warmed up to −20 °C in 3 h, then treated with methyl iodide (1 ml) and further warmed up to room temp during the period of 15 h. Workup followed by preparative TLC (silica gel, hexane, R_f 0.7—0.8) gave **2c** (19 mg, 20% yield). Any isomer was not detected by GLC or PMR assay. Bp 95—100 °C (bath temp)/24 Torr; IR (neat): 3090, 3050, 1605, 1580, 1500, 1383, 1363, 1172, 1080, 1028, 773, 734, 699 cm^{-1}; MS: *m/e* (%), 188 (M^+, 3), 131 (78), 84 (100), 69 (73), 57 (46), 41 (38); PMR (CCl_4): δ 0.66 (s, 3H, Me), 0.7—1.3 (m, 2H), 0.93 (s, 9H, *t*-Bu), 2.10 (dd, J=5, 9 Hz, 1H, PhC*H*), 6.8—7.3 (m, 5H, Ph). Found: C, 89.6; H, 11.0%. Calcd for $C_{14}H_{20}$: C, 89.3; H, 10.7%.

*1-Butyl-1-ethyl-2-phenylcyclopropanes (**2d** and **3d**).* A solution of **1a** (0.28 g, 1.0 mmol) in ether (1 ml) was added to n-Bu_2CuLi (5.0 mmol) prepared at −48 °C. Stirring was continued for 1 h and ethyl iodide (1 ml) was added. Then the mixture was gradually warmed to room temp during 15 h. Workup and preparative TLC (silica gel, hexane, R_f 0.8—0.9) afforded an isomeric mixture of **2d** and **3d** (0.14 g, 65%). Each isomer was separated by GLC (Silicone HV grease, 150 °C He, 1.7 kg/cm^2).

r-*1-Butyl-1-ethyl*-t-*2-phenylcyclopropane (**2d**)*: R_f 16 min; bp 87—95 °C (bath temp)/27 Torr; IR (neat): 3060; 3040, 1605, 1580, 1497, 1453, 1378, 1070, 1029, 774, 730, 699 cm^{-1}; MS: *m/e* (%), 202 (M^+, 18), 173 (28), 145 (100), 117 (78), 104 (52), 91 (76); PMR (CCl_4): δ 0.5—1.6 (m, 16H), 1.87 (dd, J=6, 8 Hz, 1H, PhC*H*), 6.9—7.4 (m, 5H, Ph). Found: C, 88.8; H, 10.9%. Calcd for $C_{15}H_{22}$: C, 89.0; H, 11.0%.

r-*1-Butyl-1-ethyl*-c-*2-phenylcyclopropane (**3d**)*: R_t 13 min; bp 82—89 °C (bath temp)/20 Torr; IR (neat): 3070, 3040, 1605, 1580, 1499, 1450, 1380, 1070, 1029, 778, 730 cm^{-1}; MS: *m/e* (%), 202 (M^+, 19), 173 (28), 145 (100), 117 (76),

104 (57), 91 (61); PMR (CCl_4): δ 0.5—1.6 (m, 16H), 1.82 (dd, J=6, 8 Hz, 1H, PhCH), 6.8—7.4 (m, 5H, Ph). Found: C, 88.8; H, 11.0%. Calcd for $C_{15}H_{22}$: C, 89.0; H, 11.0%.

1-Acetyl-1-butyl-2-phenylcyclopropanes (2e and 3e). A solution of **1a** (0.28 g, 1.0 mmol) in ether (1 ml) was treated with *n*-Bu_2CuLi (5.0 mmol) in ether (10 ml) at −48 °C. The reaction mixture was warmed to −20 °C during 1 h and then cooled again to −78 °C. Acetyl bromide (1.0 ml) was added and the reaction mixture was gradually warmed to room temp during 15 h. Workup and preparative TLC (silica gel, hexane–ether (4: 1) gave **2e** and **3e**.

r-*1-Acetyl-1-butyl*-c-*2-phenylcyclopropane (2e)*: R_f 0.4—0.5; bp 70—75 °C (bath temp)/0.07 Torr; IR (neat): 1690, 1600, 1580, 1498, 1450, 1355, 1196, 1134, 1025, 958, 768, 730, 695 cm^{-1}: MS: *m/e* (%), 216 (M^+, 18), 173 (26), 129 (17), 117 (19), 91 (20), 43 (100); PMR (CCl_4): δ 0.7—2.5 (m, 12H), 1.61 (s, 3H, Ac), 6.9—7.4 (m, 5H, Ph). Found: C, 83.2; H, 9.4%. Calcd for $C_{15}H_{20}O$: C, 83.3; H, 9.3%.

r-*1-Acetyl-1-butyl*-t-*2-phenylcyclopropane (3e)*: R_f 0.3—0.4; bp 66—70 °C (bath temp)/0.06 Torr; IR (neat): 1688, 1605, 1580, 1500, 1450, 1380, 1356, 1200, 1142, 778, 732, 700 cm^{-1}; MS: *m/e* (%), 216 (M^+, 16), 173 (24), 129 (13), 117 (27), 91 (19), 43 (100); PMR (CCl_4): δ 0.5—1.9 (m, 11H), 2.12 (s, 3H, Ac), 2.57 (dd, J=7, 9 Hz, 1H, PhCH), 6.9—7.3 (m, 5H, Ph). Found: C, 83.0; H, 9.5%. Calcd for $C_{15}H_{20}O$: C 83.3; H, 9.3%.

1-Butyl-2-phenylcyclopropanes (2f and 3f). A solution of **1a** (0.28 g, 1.0 mmol) in ether (1 ml) was treated with *n*-Bu_2CuLi (5.0 mmol) in ether (10 ml) at −48 °C. The reaction mixture was warmed up tp −20 °C during 1 h, and ethanol (2 ml) was added. Workup and subsequent preparative TLC purification gave a mixture of **2f** and **3f** (0.17 g, 96% yield). Each isomer was separated by preparative GLC (Silicone HV grease, 150 °C, 0.7 kg/cm^2).

trans-*1-Butyl-2-phenylcyclopropane (2f)*: R_t 12 min; bp 82—83 °C/21 Torr; IR (neat): 1605, 1500, 1465, 1084, 1020, 750, 695 cm^{-1}; MS: *m/e* (%), 174 (M^+, 22), 117 (77), 104 (100), 91 (33); PMR (CCl_4): δ 0.5—1.7 (m, 13H), 6.7—7.3 (m, 5H, Ph). Found: C, 89.5; H, 10.3%. Calcd for $C_{13}H_{18}$: C, 89.6; H, 10.4%.

cis-*1-Butyl-2-phenylcyclopropane (3f)*: R_t 11 min; bp 70—74 °C (bath temp)/4 Torr; IR (neat): 1600, 1495, 1025, 770, 723, 700 cm^{-1}; MS: *m/e* (%), 174 (M^+, 17), 117 (72), 104 (100), 91 (32); PMR (CCl_4) δ 0.4—1.7 (m, 12H), 1.7—2.3 (m, 1H), 7.0—7.2 (m, 5H, Ph). Found: C, 89.5; H, 10.7%. Calcd for $C_{13}H_{18}$: C, 89.6; H, 10.4%.

Reaction of 1,1-Dichloro-2-phenylcyclopropane (1b) with Dibutylcopperlithium. A solution of **1b** (0.19 g, 1.0 mmol) in ether (1 ml) was added to a solution of *n*-Bu_2CuLi (5.0 mmol) prepared at −48 °C, and the reaction mixture was warmed to 0 °C in 3.5 h, treated with methyl iodide (1 ml), and allowed to warm to room temp (15 h). Workup and preparative TLC afforded a mixture of **2a** and **3a** (97 mg, 71% yield) besides a recovered starting material (49 mg).

1-Iodo-1-butyl-2-phenylcyclopropane (2g and 3g). A solution of **1a** (0.28 g, 1.0 mmol) in ether (1 ml) was treated with *n*-Bu_2CuLi (5.0 mmol) in ether (10 ml) at −48 °C. The reaction mixture was warmed to −30 °C in 1 h and then treated with iodine (2.5 g, 10 mmol) dissolved in THF (4 ml), and further warmed up to room temp. Usual workup involving reduction of the excess iodine with aq. sodium thiosulfate, followed by preparative TLC (silica gel, hexane), gave **2g** (R_f 0.5—0.6, 0.16 g, 52%) and **3g** (R_f 0.6—0.7, 81 mg, 27%) along with **17c** (R_f 0.7—0.8, 22 mg, 10%).

r-*1-Iodo-1-butyl*-c-*2-phenylcyclopropane (2g)*: Bp 123—128 °C (bath temp)/3 Torr; IR (neat): 3090, 3060, 3040, 1602, 1580, 1497, 1450, 1370, 1150, 1022, 780, 756, 722, 690 cm^{-1}; MS: *m/e* (%), 300 (M^+, 2), 217 (5), 173 (38), 131 (22), 117 (100) 91 (68); PMR (CCl_4): δ 0.6—2.2 (m, 12H), 6.8—7.4 (m, 5H, Ph). Found: C, 52.3; H, 5.8%. Calcd for $C_{13}H_{17}I$: C, 52.0; H, 5.7%.

r-*1-Iodo-1-butyl*-t-*2-phenylcyclopropane (3g)*: Bp 118—124 °C (bath temp)/3 Torr; IR (neat): 3090, 3070, 3040, 1600, 1580, 1499, 1450, 1370, 1195, 1142, 770, 725, 695 cm^{-1}; MS: *m/e* (%), 300 (M^+, 2), 217 (1), 173 (37), 131 (23), 117 (100), 91 (68); PMR (CCl_4): δ 0.5—1.8 (m, 11H), 2.78 (dd, J=7, 10 Hz, 1H, PhC*H*), 7.0—7.4 (m, 5H, Ph). Found: C, 52.3; H, 5.8%. Calcd for $C_{13}H_{17}I$: C, 52.0; H, 5.7%.

1,1-Dibutyl-2-phenylcyclopropane (17c): Bp 80—86 °C (bath temp)/2 Torr; IR (neat): 3040, 1600, 1495, 1460, 1027, 780, 727, 700 cm^{-1}; MS: *m/e* (%), 230, (M^+, 17), 173 (66), 117 (100), 104 (55), 91 (68); PMR (CCl_4): δ 0.5—1.7 (m, 20H), 1.83 (dd, J=7, 10 Hz, 1H, PhC*H*), 6.8—7.3 (m, 5H, Ph). Found: C, 88.4; H, 11.4%. Calcd for $C_{17}H_{26}$: C, 88.6; H, 11.4%.

Air Oxidation of the Cyclopropylcopper Reagent Prepared from **1a** *and Dibutylcopperlithium.* A solution of **1a** (0.28 g, 1.0 mmol) in ether (1 ml) was treated with *n*-Bu_2CuLi (5.0 mmol) in ether (10 ml) at −48 °C. After 1 h dry air (passed through $CaCl_2$ and silica gel) was introduced into the reaction mixture which was subsequently allowed to warm to 0 °C in 3 h. Workup and subsequent TLC purification (silica gel, hexane) gave **17c** (R_f 0.7—0.8, 80 mg, 34%), **3g** (R_f 0.6—0.7, 38 mg, 12%), and **2g** (R_f 0.5—0.6, 54 mg, 18%).

1-Butyl-1-methyl-2-hexylcyclopropane (2h and 3h). Dibromocyclopropane **1c** (0.30 g, 1.0 mmol) in ether (1 ml) was treated with *n*-Bu_2CuLi (5.0 mmol) in ether (10 ml) at −48 °C to −20 °C for 1 h. Addition of methyl iodide (1 ml) at −20 °C, followed by usual workup and preparative TLC (silica gel, hexane, R_f 0.8—0.9), gave a mixture of **2h** and **3h** (0.10 g, 50% yield). Each product was separated by GLC (Silicone HV grease, 150 °C, 0.8 kg/cm^2).

r-*1-Butyl-1-methyl*-t-*2-hexylcyclopropane (2h)*: R_t 58 min; bp 75—80 °C (bath temp)/4 Torr; IR (neat): 3050, 2930 2860, 1465, 1375, 1020, 730 cm^{-1}; MS: *m/e* (%), 196 (M^+, 4) 154 (6), 139 (11), 126 (4), 111 (8), 97 (24), 83 (55), 69 (98), 55 (100); PMR (CCl_4): δ −0.3—0.5 (m, 3H), 0.97 (s, 3H, Me), 0.7—1.9 (m, 22H). Found: C, 85.8; H, 14.5%. Calcd for $C_{14}H_{28}$: C, 85.6; H, 14.4%.

r-*1-Butyl-1-methyl*-c-*2-hexylcyclopropane (3h)*: R_t 38 min; bp 60—65 °C (bath temp)/3 Torr; IR (neat): 3050, 2930, 1460, 1370, 1255, 1015 cm^{-1}; MS: *m/e* (%), 196 (M^+, 3), 154 (5), 139 (8), 126 (3), 111 (11), 97 (17), 83 (41), 69 (79), 55 (78), 44 (100); PMR (CCl_4): δ −0.3—0.6 (m, 3H), 0.99 (s, 3H, Me), 0.6—1.7 (m, 22H). Found: C, 85.6; H, 14.4%. Calcd for $C_{14}H_{28}$: C, 85.6; H, 14.4%.

1-Butyl-1-methyl-2-benzyloxymethylcyclopropanes (2i and 3i). A solution of **1d** (0.32 g, 1.0 mmol) in ether (1 ml) was treated with *n*-Bu_2CuLi (5.0 mmol) in ether (10 ml) at −48 °C. The reaction mixture was gradually warmed up to −20 °C during 1 h and treated with methyl iodide (1 ml), and then further warmed to room temp in 15 h. Workup and preparative TLC (silica gel, hexane–ether 1: 1) gave a mixture of **2i** and **3i** (0.12 g, 50% yield). Each product was separated by preparative GLC (Apiezon L (30%) and KOH (10%) on Chromosorb W, 2 m, 150 °C, 1.0 kg/cm^2 of He gas).

r-*1-Butyl-1-methyl*-t-*2-benzyloxymethylcyclopropane (2i)*: R_t 35 min; bp 73—80 °C (bath temp)/0.06 Torr; IR (neat): 1492, 1450, 1374, 1254, 1090, 1025, 790, 734, 700 cm^{-1}; MS: *m/e* (%), 232 (M^+, 0.2), 217 (0.1), 191 (2), 188 (1), 175 (2), 91 (100); PMR (CCl_4): δ 0.3—0.6 (m, 1H), 0.7—1.7 (m, 11H), 1.03 (s, 3H, Me), 3.17 (dd, J=8, 10 Hz, 1H, OCH_aH_b), 3.53 (dd, J=6, 10 Hz, 1H, OCH_aH_b), 4.43 (s, 2H, $PhCH_2$), 7.2—7.3 (m, 5H, Ph). Found: C, 82.9; H, 10.6%. Calcd

for $C_{16}H_{24}O$: C, 82.7; H, 10.4%.

r-*1-Butyl-1-methyl*-c-*2-benzyloxymethylcyclopropane (3i)*: R_t 30 min; bp 75—83 °C (bath temp)/0.06 Torr; IR (neat): 1494, 1451, 1375, 1255, 1090, 1027, 805, 736, 700 cm^{-1}; MS: *m/e* (%), 232 (M^+, 0.05), 217 (0.1), 191 (0.5), 188 (0.5), 175 (0.5), 91 (100); PMR (CCl_4): δ 0.3—0.5 (m, 1H), 0.7—1.7 (m, 11H), 1.03 (s, 3H, Me), 3.22 (dd, J=8, 10 Hz, 1H, OCH_aH_b), 3.50 (dd, J=6, 10 Hz, 1H, OCH_aH_b), 4.41 (s, 2H, $PhCH_2$), 7.2—7.4 (m, 5H, Ph). Found: C, 82.6; H, 10.5%. Calcd for $C_{16}H_{24}O$: C, 82.7; H, 10.4%.

7-exo-*Butyl-7*-endo-*methylnorcarane (2j)*. A solution of 7,7-dibromonorcarane (**1e**) (0.26 g, 1.0 mmol) in ether (1 ml) was treated with *n*-Bu_2CuLi (5.0 mmol) in ether (10 ml) at −48 °C. After 1 h methyl iodide (1.0 ml) was added and the reaction mixture was gradually warmed up to room temp in 3 h. Workup and subsequent preparative TLC (silica gel, hexane, R_f 0.8—0.9) afforded **2j** (0.14 g, 82% yield). Bp 100—106 °C (bath temp)/15 Torr; IR (neat): 3000, 1465, 1449, 1380, 785 cm^{-1}; MS: *m/e* (%), 166 (M^+, 5), 152 (3), 151 (3), 123 (9), 110 (54), 109 (100), 95 (26); PMR (CCl_4): δ 0.4—0.6 (m, 2H), 0.93 (s, 3H, Me), 0.6—2.6 (m, 17H). Found: C, 86.6; H, 13.6%. Calcd for $C_{12}H_{22}$: C, 86.7; H, 13.3%.

exo-*7-Butyl*-endo-*7-methylnorcaran-2-one (2k)*. Dichlorocarbene adduct **1f** (0.22 g, 1.0 mmol) in ether (1 ml) was treated with *n*-Bu_2CuLi (5.0 mmol) in ether (10 ml) at −48 °C to 0 °C for 3 h and at 0 °C for 1 h. After the addition of methyl iodide (1 ml) the reaction mixture was gradually warmed to room temp (3 h). Workup and concentration *in vacuo* afforded an oil which was subsequently treated with a mixture of THF (1 ml) and 1.5 M aq H_2SO_4 at room temp for 1 h. Workup and subsequent TLC (silica gel, hexane–ether 3:1, R_f 0.3—0.4) afforded **2k** (0.14 g, 78% yield). Bp 90—97 °C (bath temp)/15 Torr; IR (neat): 1690, 1470, 1320, 1240, 1180, 1110, 890 cm^{-1}; MS: *m/e* (%), 180 (M^+, 8), 124 (42), 95 (100), 82 (84); PMR (CCl_4): δ 0.6—2.6 (m, 17H), 1.09 (s, 3H, Me). Found: C, 80.0; H, 11.3%. Calcd for $C_{12}H_{20}O$: C, 79.9; H, 11.2%.

exo-*7-(4-Methyl-3-pentenyl)*-endo-*7-methylnorcaran-2-one (6)*. An ethereal solution of 4-methyl-3-pentenyllithium (14 ml of 0.86 M solution, 12 mmol) was added to cuprous iodide (1.1 g, 6.0 mmol) suspended in a mixture of hexane (15 ml) and ether (5 ml) at −78 °C. During the period of 40 min the reaction mixture was warmed to −70 °C and then a solution of **1f** (0.27 g, 1.2 mmol) in ether (1 ml) was added to the resulting dark gray slurry. The reaction mixture was gradually warmed to −20 °C in 1 h, treated with methyl iodide (2 ml) and allowed to warm to room temp (16 h). Usual workup gave an oil which was subsequently treated with a mixture of THF (1 ml) and 1.5 M aq H_2SO_4 (1 ml) at room temp for 40 min. Workup and preparative TLC purification (silica gel, CH_2Cl_2, R_f 0.3—0.4) gave **6** (0.11 g, 44%). Bp 95—105 °C (bath temp)/0.1 Torr; IR (neat): 1685, 1445, 1380, 1349, 1330, 1245, 895, 790 cm^{-1}; MS: *m/e* (%), 206 (M^+, 5), 137 (22), 69 (87), 41 (100); PMR (CCl_4): δ 1.115 (s, 3H, Me), 1.59 (s, 3H, Me), 1.67 (s, 3H, Me), 1.2—2.3 (m, 12H), 4.9—5.2 (m, 1H). The product **6** was converted into 3-carbomethoxy-*exo*-7-(4-methyl-3-pentenyl)*endo*-7-methylnorcaran-2-one (**7**) according to the literature.[7a] Bp 110—120 °C (bath temp)/0.3 Torr; IR (neat): 1744, 1689, 1644, 1610 cm^{-1}; MS: *m/e* (%), 264 (M^+, 3), 69 (82), 55 (48), 41 (100); PMR: Fig. 1.

Authentic Samples of 2h and 3h. A solution of 3-methylhept-2-en-1-ol (**9**) (0.74 g, 5.7 mmol, *E*: *Z* 80:20) in ether (5 ml) was treated with phosphorous tribromide (0.52 g, 1.9 mmol) at −78 °C. The solution was stirred at room temp for 3 h and worked up. Distillation (80—90 °C/18 Torr) of the crude product gave 1-bromo-3-methylhept-2-ene (0.78 g, 71%). The bromide was directly treated with amylmagnesium bromide (5.0 mmol) in ether (4 ml) at room temp for 2 h. Workup and GLC separation (Silicone HV grease, 150 °C, 0.8 kg/cm^2, R_t 30 min) gave an isomeric mixture of 5-methyl-5-dodecene (**10**) (15 mg, *E*: *Z* 82:18), which was converted to a mixture of **2h** and **3h** (ratio 84:16) upon heating with methylene iodide (85 mg, 0.32 mmol), zinc powder (42 mg, 0.64 mmol), and cuprous chloride (10 mg, 0.10 mmol) for 15 h.[10] GLC separation of the products gave the authentic samples of **2h** and **3h**, both of which showed the identical GLC retention times (5% Apiezon L grease and 1% KOH on Chromosorb W, 2 m, 104 °C, 0.6 kg/cm^2; R_t of **2h**, 27 min; R_t of **3h**, 25 min) and MS spectra with the samples prepared by the cuprate reaction.

Authentic Samples of 2i and 3i. The allyl alcohol **9** (0.13 g, 1.0 mmol, *E*: *Z* 80:20) was transformed, upon heating with methylene iodide (0.41 g, 1.5 mmol), zinc powder (0.20 g, 3.0 mmol) and cuprous chloride (30 mg, 0.30 mmol) in ether (2 ml) for 15 h,[10] to the cyclopropyl carbinol **11**: bp 85—95 °C (bath temp)/56 Torr; IR (neat): 3340, 1020 cm^{-1}: MS: *m/e* 124 (M^+-H_2O); PMR (CCl_4): δ 1.05 (s, 3H, Me), 3.1—3.8 (m, 2H, CH_2O). The crude cyclopropyl carbinol **11** in *N,N*-dimethylformamide (DMF) (0.5 ml) was mixed with sodium hydride (50 mg) in DMF (1 ml) and the whole was stirred at room temp for 1 h, treated with benzyl chloride (0.15 ml) and worked up after 30 min. Preparative TLC of the crude product (silica gel, ether–hexane 1:3, R_f 0.8) gave a mixture of **2i** and **3i** (92 mg, 40% overall yield from **9**, 76:28 ratio). GLC separation afforded each isomer which was identical with the samples prepared by cuprate reaction.

Authentic Samples of 2k. A solution of **12** (0.76 g, 3.7 mmol, *E*: *Z* 77:23) in ethanol (1 ml) was treated with diethyl sodiomalonate (prepared from 1.2 g of diethyl malonate, 7.4 mmol) according to the literature.[7d] Workup and short path distillation at 124—134 °C/6 Torr gave crude diethyl 4-methyl-3-octenylmalonate (0.49 g) which was directly hydrolyzed (KOH, ethanol reflux) and decarboxylated (acetic acid, reflux for 2 days).[7d] Short path distillation at 106—116 °C/4 Torr gave 6-methyl-5-decenoic acid (**13**) (0.24 g); IR (neat): 3600—3200, 1710, 1410, 1240, 930 cm^{-1}; PMR (CCl_4): δ 1.60 and 1.68 (s, 3H, vinylic methyl of *E* and *Z* isomers), 5.06 (t, J=6 Hz, 1H); *E*: *Z* 70:30. The acid **13** (0.24 g, 1.3 mmol) was heated with $SOCl_2$ (0.18 g, 1.5 mmol) in dry benzene (5 ml) to reflux for 1 h and the mixture was concentrated. The residue was distilled at 90—100 °C/0.2 Torr and the distillate was treated with excess diazomethane in ether at 0 °C and left over night. The solvent and the excess diazomethane were removed by passing a nitrogen stream over the surface. The concentrated crude diazoketone **14** was dissolved in cyclohexane (1 ml) and added dropwise to a suspension of cupric sulfate (0.30 g, 1.9 mmol) in refluxing cyclohexane (110 ml). After 2 h reflux the reaction mixture was filtered and concentrated *in vacuo*. Short path distillation of the residue at 100—115 °C/5 Torr afforded an oil (0.18 g, 78% overall yield from **13**). Although the product showed identical IR and MS spectra with that of **2k** prepared by cuprate reaction, GLC (3% Apiezol L grease and 10% KOH on Neosorb NC, 154 °C, 1.0 kg/cm^2 of He) and PMR revealed that it was a mixture (71:29) of **2k** (R_t 6.9 min, methyl signal at δ 1.09) and its stereoisomer (R_t 5.6 min, methyl signal at δ 1.11).

Authentic Samples of 2j. A mixture of **2k** (0.14 g, 0.78 mmol), 80% hydrazine hydrate (3.2 g, 51 mmol) and hydrazine dihydrochloride (0.65 g, 6.2 mmol) in triethylene glycol (15 ml) was heated at 130 °C. After 3 h potassium hydroxide

(0.96 g, 17 mmol) was added and the mixture was heated at 210 °C for 3 h during which volatile products were distilled off. Preparative TLC (silica gel, hexane) of the distillate gave an oil (R_f 0.9, 24 mg) which was further purified by preparative GLC (Silicone HV grease, 130 °C, He, 0.8 kg/cm^2) giving an authentic sample of **2j**.

Reaction of ***1a*** *with Dimethylcopperlithium in Ether.* Methyllithium (20 ml of 0.5 M ether solution, 10 mmol) was added to cuprous iodide (0.95 g, 5.0 mmol) suspended in ether (5 ml) and hexane (15 ml) at 0 °C. After cooling to −38 °C **1a** (0.28 g, 1.0 mmol) in ether (1 ml) was added and the reaction mixture was gradually warmed to 0 °C in 3 h. Workup and preparative TLC (silica gel, hexane) afforded 1,1-dimethyl-2-phenylcyclopropane (**17a**) (R_f 0.6—0.7, 26 mg, 17%) and a mixture of **15a** (R_f 0.4—0.5, 46 mg, 21%) and **16a** (R_f 0.5—0.6, 60 mg, 28%). Physical properties of **17a**: bp 69—76 °C (bath temp)/20 Torr; IR (neat): 1609, 1580, 1499, 1451, 1375, 1028, 779, 730, 700 cm^{-1}; MS: *m/e* (%), 146, (M$^+$, 38), 131 (100), 117 (20), 91 (50); PMR (CCl_4): δ 0.5—2.0 (m, 3H), 0.78 (s, 3H, Me), 1.22 (s, 3H, Me), 6.7—7.3 (m, 5H, Ph). Found: C, 90.6; H, 9.4%. Calcd for $C_{11}H_{14}$: C, 90.4; H, 9.7%.

Conversion of ***1a*** *to* ***17a***. A solution of methyllithium (3.2 ml of 1.9 M ether solution, 6.0 mmol) was added to a suspension of cuprous iodide (0.58 g, 3.0 mmol) in THF (10 ml) at 0 °C. The reaction mixture was cooled at −78 °C, treated with **1a** (0.28 g, 1.0 mmol) in THF (1 ml) and warmed to room temp in 15 h. Workup and preparative TLC (silica gel, hexane, R_f 0.7—0.8) afforded **17a** (69 mg, 48% yield).

Reaction of ***1a*** *with Divinylcopperlithium.* A solution of vinyllithium (35 ml of 0.85 M ether solution, 30 mmol) was added to a suspension of cuprous iodide (2.9 g, 15 mmol) in hexane (18 ml) at −48 °C. After 5 min the cuprate solution was cooled to −78 °C and a solution of **1a** (1.4 g, 5.0 mmol) in hexane (2 ml) was added. After 2 h the reaction mixture was quenched with ethanol (1 ml) and allowed to warm to room temp. Workup and subsequent preparative TLC (silica gel, hexane) afforded **15b** and **16b**.

r-*1-Bromo-c-2-phenyl-1-vinylcyclopropane (**15b**)*: R_f 0.7—0.8, 0.23 g, 20% yield; bp 80—87 °C (bath temp)/3 Torr; IR (neat): 1630, 1604, 1500, 1450, 1120, 1020, 970, 903, 698 cm^{-1}; MS: *m/e* (%), 222 (M$^+$, 1), 195 (1), 143 (89), 141 (24), 128 (100), 115 (35), 91 (24), 65 (15); PMR (CCl_4): δ 1.5—1.9 (m, 2H), 2.23 (dd, J=8, 10 Hz, 1H, PhCH), 4.9—6.1 (m, 3H), 7.0—7.4 (m, 5H, Ph). Found: C, 59.2; H, 4.9%. Calcd for $C_{11}H_{11}Br$: C, 59.2; H, 5.0%.

r-*1-Bromo-t-2-phenyl-1-vinylcyclopropane (**16**)*: R_f 0.8—0.9, 0.66 g, 59%; bp 75—82 °C (bath temp)/2 Torr; IR (neat): 1630, 1602, 1496, 1450, 1160, 970, 903, 697 cm^{-1}; MS: *m/e* (%), 222 (M$^+$, 1), 195 (1), 143 (86), 141 (26), 128 (100), 115 (45), 91 (21), 65 (16); PMR (CCl_4): δ 1.4—2.0 (m, 2H), 2.91 (dd, J=8, 9 Hz, 1H, PhC*H*), 4.9—5.5 (m, 3H), 7.0—7.3 (m, 5H, Ph). Found: C, 59.3; H, 5.0%. Calcd for $C_{11}H_{11}Br$: C, 59.2; H, 5.0%.

*1-Phenyl-2,2-divinylcyclopropane (**17b**)*. A solution of **1a** (0.14 g, 0.50 mmol) in ether (0.5 ml) was added to a solution of divinylcopperlithium (2.5 mmol) in a mixture of ether (6 ml) and hexane (4 ml) at −48 °C. The reaction mixture was gradually warmed to 0 °C during the period of 3 h. Workup followed by preparative TLC (silica gel, hexane, R_f 0.3—0.4) gave **17b** (40 mg, 47%). Bp 61—66 °C (bath temp)/3 Torr; IR (neat): 1634, 1623, 1600, 1492, 985, 895, 773, 733, 695 cm^{-1}; MS: *m/e* (%), 170 (M$^+$, 58), 155 (82), 141 (46), 128 (85), 115 (80), 91 (100); PMR (CCl_4): δ 0.8—1.7 (m, 2H), 2.35 (dd, J=6, 9 Hz, 1H, PhC*H*), 4.7—6.3 (m, 6H), 6.9—7.3 (m, 5H, Ph). Found: C, 91.9; H, 8.4%. Calcd for $C_{13}H_{14}$: C, 91.7; H, 8.3%.

trans-*1-Allyl-2-phenylcyclopropane (**20**)*. A solution of *n*-BuLi (7.2 ml of 1.7 M hexane solution, 12 mmol) was added slowly to a stirred suspension of cuprous iodide (1.1 g, 6.0 mmol) in THF (20 ml) at −48 °C. After 10 min a solution of *trans*-1-bromo-2-phenylcyclopropane (**19**) (0.29 g, 1.5 mmol) in THF (2 ml) was added and stirring was continued further 49 min at this temp. Allyl bromide (1.5 ml) in HMPA (1 ml) was then added and after 30 min the reaction mixture was worked up as usual. Preparative TLC (silica gel, hexane, R_f 0.3—0.4) of the crude oil gave **20** (0.22 g, 97%). Bp 55—60 °C (bath temp)/15 Torr; IR (neat): 1639, 1605, 1497, 1460, 1030, 995, 913, 790, 756, 700 cm^{-1}; MS: *m/e* (%), 158 (M$^+$, 6), 143 (4), 129 (9), 117 (100), 104 (36), 91 (35); PMR (CCl_4): δ 0.6—1.5 (m, 3H), 1.5—1.9 (m, 1H, PhCH), 2.0—2.4 (m, 2H, allylic H), 4.9—6.3 (m, 3H), 6.8—7.4 (m, 5H). Found: C, 90.8; H, 9.0%. Calcd for $C_{12}H_{14}$: C, 91.1; H, 8.9%.

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