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Alkylation of Bromocyclopropanes and Bromoarenes by Means of Dibutylcopperlithium and Alkyl Halides

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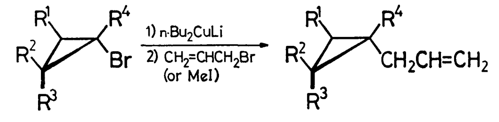
Treatment of bromocyclopropanes with excess dibutylcopperlithium in tetrahydrofuran at −48 °C gives the respective organocopper intermediates which upon quenching with excess alkyl halides afford alkylated cyclopropanes with retention of the configuration. This process is applied to the synthesis of methyl cascarillate. Bromoarenes are also reduced with dibutylcopperlithium and allylarenes are prepared therefrom.

Organocopper reagents are widely used for C–C bond formation including addition reaction to unsaturated compounds[1] and coupling reaction with organic halides, tosylates, acetates and epoxides.[2] Synthetically versatile is the alkylation reaction of organocuprates (dialkylcoppermetals). Stereochemical studies have stimulated arguments on the mechanism of alkylation,[2] *i.e.* S_N2 like alkyl transfer pathway or oxidative addition followed by reductive coupling pathway. In both cases the ligand of the copper reagent and organic residue of substrates combine to give the alkylated products. The third mechanism is transmetallation suggested earlier by Whitesides *et al.*[3] for the reaction of dialkylcopperlithium (R_2CuLi) and aryl haldies (ArX), wherein a mixed homocuprate (ArCuRLi) is initially formed which subsequently gives an equilibrium mixture (Ar_2CuLi, ArCuRLi, R_2CuLi) of cuprates.[2] Therefore this process has been of no synthetic value. However, the synthetic utility of the transmetallation is suggested recently in the *gem*-dialkylation of 1,1-dibromocyclopropanes with dialkylcopperlithium.[4] This process involving a cyclopropylcopper intermediate is now proved to be general and useful especially for the stereocontrolled synthesis of substituted cyclopropanes.[5]



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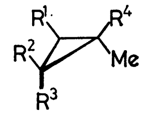

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	R^1	R^2	R^3	R^4
a	H	C_6H_5	H	H
b	H	H	C_6H_5	H
c	H	C_6H_5	H	CH_3
d	H	n-C_6H_{13}	H	H
e	H	$C_6H_5CH_2OCH_2$	H	H
f	$-(CH_2)_4-$		H	H
g	$-(CH_2)_4-$		H	$CH_2CH=CH_2$
h	$-(CH_2)_4-$		CH_3	H

Bromocyclopropanes **1a**—**1h** were stereoselectively prepared by protonating or alkylating the carbenoid derived from the corresponding *gem*-dibromide.[6] When bromocyclopropane **1** was treated with 4 to 5 equivalents of dibutylcopperlithium in tetrahydrofuran (THF) at −48 °C to 0 °C, the starting bromide was all consumed. Quenching with excess allyl bromide (or methyl iodide) at the same temperature afforded allylcyclopropane **2** (or methylcyclopropane **3**) in good yield. The results are summarized in Table 1. In sharp contrast to the

TABLE 1. ALKYLATION OF BROMOCYCLOPROPANE **1**

Bromocyclopropane (mg) (mmol)	Dibutylcopper-lithium(mmol)	Alkyl halide[a] (ml)	Temp of alkylation (°C)	Product yield[b] (mg) (%)
1a (289) (1.5)	6.0	A (1.5)	−48	**2a**[c] (224) (97)
1a (193) (1.0)	4.0	M (1.0)	−48	**3a** (117) (91)
1a (294) (1.5)	6.0	A (1.0)	−48	**6**+**7** (269) (97)[d]
1b (131) (0.66)	2.7	A (0.8)	−48	**2b** (96) (91)
1c (199) (0.94)	3.8	A (1.0)	0	**2c** (111) (68)[e]
1d[f] (411) (2.0)	10	A (1.5)	−48	**2d**[g] (319) (96)
1e (360) (1.5)	6.0	A (1.5)	−48	**2e** (197) (65)
1f (264) (1.5)	6.0	A (1.5)	−48	**2f** (119) (57)
1g (217) (1.0)	5.0	M (1.0)	0	**3g** (145) (96)
1h (199) (1.0)	5.0	A (1.5)	0	**2h** (102) (65)
1h (152) (0.80)	5.0	O (1.0)[h]	0	**4** (−) (50)[i]

a) A: allyl bromide, M: methyl iodide, O: octyl bromide. b) Yield of purified product unless otherwise stated. c) The stereochemical assignment is based on the general observation that PMR absorption of the substituent cis to the phenyl group appears at higher field than that of the trans isomer. See Ref. 6. d) A 7 : 3 mixture of **6** and **7**. e) *r*-1-Butyl-1-methyl-*t*-2-phenylcyclopropane (Ref. 4) was a by-product (36mg, 20%). f) An 83 : 17 mixture of **1d** and its cis isomer. g) An 84 : 16 mixture of **2d** and its cis isomer. h) Octyl bromide dissolved in HMPA (1 ml) was added. In the absence of HMPA the yield of **4** was *ca.* 30%. i) The yield was estimated by GLC.

conventional alkylation of organic halides with dibutylcopperlithium, no trace of butylated products were formed in the present reaction.

The salient features of this alkylation process are:

(1) The net retention of configuration is observed in the allylation of **1a** and **1b** furnishing **2a** and **2b** respectively as the sole product.

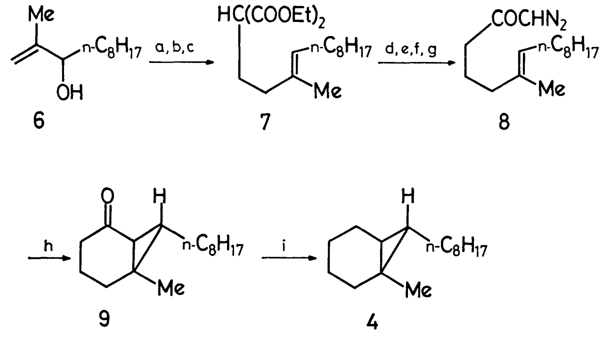
(2) Even tertiary halides (*e.g.* **1c** and **1g**) are alkylated to give the *gem*-dialkylated cyclopropanes. Thus, the two different alkyl groups are introduced both as electrophiles in contrast to the previous method.[4]

(3) The reaction reported here is sometimes more efficient than that which employs bromine-lithium exchange reaction.[7] Treating **1a** with *t*-butyllithium and then with excess allyl bromide gave only a 23% yield of **2a**. The *exo*-bromonorcarane derivative **1h** did not afford **2h** in the organolithium reaction.

(4) As the bromocyclopropanes are not reduced in ether, the highly coordinating THF is indispensable for the reaction.

(5) Control experiments using **1h** as the substrate revealed that at least 3.5 mol of dibutylcopperlithium is required for the complete consumption of **1h**. All attempts to reduce **1a** with *n*-Bu(PhS)CuLi (2 mol), *n*-Bu(*i*-Pr_2N)CuLi (2 mol) or *t*-Bu_2CuLi (4 mol) failed and the recovery of the starting bromide was observed. Although an excess of dibutylcopperlithium (generally 4 to 5 mol) is required for the bromocyclopropanes and the excess cuprate also reacts with alkyl halides, such by-products are fortunately removed readily by simple distillation or chromatography.

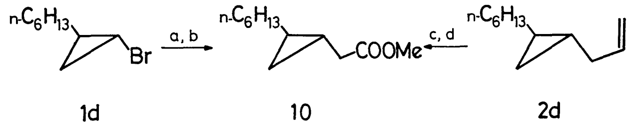
(6) Alkylation of **1h** by use of an unactivated bromide such as octyl bromide turned out rather sluggish. The yield was somewhat improved by adding hexamethylphosphoric triamide (HMPA) as the cosolvent. The stereochemistry of the product was unambiguously determined by the synthesis of the authentic specimen as shown in Scheme 1.



a: CH_2I_2, Zn–CuCl; b: 48% HBr: c: $NaCH(COOEt)_2$; d: OH^-; e: AcOH; f: $SOCl_2$; g: CH_2N_2; h: $CuSO_4$–Cu, Δ; i: N_2H_4, KOH.

Scheme 1.

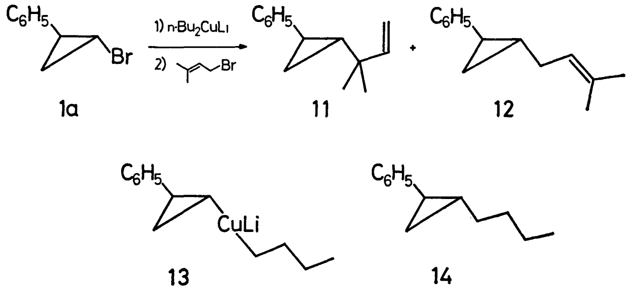
(7) Dibutylcopperlithium treatment of **1d** followed by alkylation with methyl bromoacetate gave methyl cascarillate (**10**),[8] a component of an essential oil of *Croton eluteria* Benett. This compound was alternatively obtained by permanganate-periodate oxidation of **2d** followed by esterification. The resulting ester was completely identical with the authentic sample spectrometrically and chromatographically.



a: *n*-Bu_2CuLi; b: $BrCH_2COOMe$; c: $KMnO_4$–$NaIO_4$; d: CH_2N_2.

(8) Alkylation by means of vinyl bromide was very slow and this reaction turned out futile practically.

Following experiments serve to give insight of the reaction intermediates. Metallation of **1a** and quenching with 3-methyl-2-butenyl bromide gave an S_N2' coupling product **11** mainly. Treatment with benzoyl chloride yielded *trans*-1-benzoyl-2-phenylcyclopropane (95%)and the reaction with methyl propiolate gave methyl *trans*-3-(2-phenylcyclopropyl)acrylate (46%), whereas attempted reaction with benzaldehyde gave only a 26% yield of the adduct and the one with acetone failed to succeed. Decomposition of the intermediary species occurred at 60 °C to give phenylcyclopropane (56%), while oxidation with air yielded *trans*-1-butyl-2-phenylcyclopropane (**14**)[9] (60%). These results favor a mixed homocuprate **13** as an intermediate which is ascribed to the C–Cu bond formation with retention of configuration. Such bromine-copper exchange reaction is not unprecedented.[3] However, it should be noted that butyl-cyclopropyl coupling is almost completely suppressed in **13**. Discrete existence of such mixed cuprate is suggested recently in the reaction of propargyl acetate with dimethylcopperlithium at low temperature.[10]



The reaction of *cis*-1-chloro-2-phenylcyclopropane with dibutylcopperlithium took 4 days at room temperature, and the product proved to be **14**. GLC monitoring revealed that chlorine was directly substituted with butyl group in sharp contrast to the reaction of **1a**. It is noteworthy that the substitution occurs under inversion.

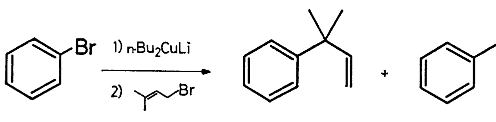
Bromoarenes underwent the Br–Cu exchange reaction under the same conditions in sharp contrast to the results by Whitesides *et al.*[3] who used ether as the solvent. Upon quenching with allyl bromide allylarenes were produced in good yields. For example, bromobenzene was treated successively with dibutylcopperlithium and allyl bromide to give allylbenzene in 64% isolated yield. Some results are listed in Table 2. HMPA cosolvent improved somewhat the yield of the allylated products. Again butylbenzene was not produced to any extent, and **15** and **16** were produced

TABLE 2. ALLYLATION OF BROMOARENES[a)]

Bromoarene (mg) (mmol)	Allyl bromide[b)] (1.0 ml each)	Product yield[c)] (mg) (%)
C_6H_5Br (157) (1.0)	A	$C_6H_5CH_2$–CH=CH_2 (77) (64)
C_6H_5Br (158) (1.0)	B	**15**+**16** (100) (68)[d)]
C_6H_5Br (157) (1.0)	B[e)]	**15**+**16** (113) (77)[f)]
C_6H_5I (204) (1.0)	B[e)]	**15**+**16** (88) (60)[f)]
1-Bromonaphthalene (200) (0.97)	A[e)]	1-Allylnaphthalene (122) (75)

a) Dibutylcopperlithium (4.0 mmol) was used for haloarene (1.0 mmol). b) A: allyl bromide. B:3-methyl-2-butenyl bromide. c) Isolated yield. d) 73: 27. e) Dissolved in HMPA (2 ml). f) 70: 30.

in the reaction with 3-methyl-2-butenyl bromide, the S_N2' product **15** being the major one. Thus the mixed cuprate of type ArCu(*n*-Bu)Li apparently is an intermediate responsible for the observed reactivity. The s character of C–Br bond is the key for the Br–Cu exchange reaction.



15 16

Experimental

All the reactions were carried out under an argon atmosphere and the temperatures are uncorrected. The cold bath of −48 °C was prepared by mixing Dry Ice with *m*-xylene. The IR spectra were recorded on a Shimadzu spectrometer 27-G, MS on a Hitachi RMU-6L, and PMR on a JEOL JNM-PMX 60 or Varian EM 390 spectrometer. Butyllithium was purchased from Aldrich Chemical Co. Ltd. Tetrahydrofuran (THF) was dried on benzophenone ketyl and freshly distilled before use.

Standard Procedure for Dibutylcopperlithium Reduction of Cyclopropyl Bromides and Alkylation. Butyllithium hexane solution (1.65 M, 7.2 ml, 12.0 mmol) was added over 5 min period at −48 °C to a suspension of copper(I) iodide (1.13 g, 6.0 mmol) in THF (20 ml) under an argon atmosphere. After 10 min cyclopropyl bromide (1.5 mmol) in THF (2 ml) was added to the resulting black solution of dibutylcopperlithium, and the reaction mixture was stirred further for 30 min, then treated with excess of an electrophile. After 30 min the reaction mixture was quenched at −48 °C with methanol (1 ml), diluted with aq sat. ammonium chloride and extracted with ether. Product was purified by prepararative TLC.

trans-*1-Allyl-2-phenylcyclopropane (2a)*: Bp 55—60 °C (bath temp)/15 Torr. PMR (CCl_4): δ 0.6—1.5 (m, 3H), 1.5—1.9 (m, 1H), 2.0—2.4 (m, 2H), 4.9—6.3 (m, 3H), 6.8—7.4 (m, 5H); IR (neat): 1639, 1605, 1030, 995, 913, 790, 756, 700 cm^{-1}; MS *m/e* (rel intensity): 156 (M^+, 6), 117 (100), 104 (36), 91 (35). Found: C, 90.84; H, 9.01%. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92%.

cis-*1-Allyl-2-phenylcyclopropane (2b)*: Bp 70—75 °C (bath temp)/20 Torr; PMR (CCl_4): δ 0.5—2.4 (m, 6H), 4.7—6.0 (m, 3H), 7.10 (s, 5H); IR (neat): 1640, 1605, 1501, 1026, 990, 910 cm^{-1}; MS *m/e* (rel intensity): 158 (M^+, 4), 117 (83), 115 (100), 104 (35), 91 (23). Found: C, 90.80; H, 9.15%. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92%.

r-*1-Allyl-1-methyl*-t-*2-phenylcyclopropane (2c)*: Bp 60—63 °C (bath temp)/14 Torr; PMR (CCl_4): δ 0.7—0.9 (m+s (δ 0.75), 5H), 1.7—2.3 (m, 3H), 4.8—5.3 (m, 2H), 5.5—6.3 (m, 1H), 7.12 (s, 5H); IR (neat): 3060, 1640, 1604, 1500, 1068, 1022, 992, 912, 790, 700 cm^{-1}; MS *m/e* (rel intensity): 172 (M^+, 1), 131 (100), 104 (17), 91 (39). Found: C, 90.34; H, 9.52%. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36%.

trans-*1-Allyl-2-hexylcyclopropane (2d).* A THF (2 ml) solution of **1d** and its cis isomer[6)] (83: 17 as assayed by GLC) (411 mg, 2.0 mmol) was added to dibutylcopperlithium (10 mmol) in THF (30 ml) at −48 °C. After 30 min allyl bromide (1 ml) was added, and 30 min thereafter the reaction mixture was worked up. Preparative TLC (silica gel, hexane, R_f 0.7—0.9) of the crude product gave a mixture of **2d** and its cis isomer (84: 16 as revealed by GLC) (319 mg, 96% yield). Each product was separated and characterized. **2d**: bp 70—75 °C (bath temp)/20 Torr; PMR (CCl_4): δ 0.0—0.6 (m, 4H), 0.6—1.7 (m, 13H), 1.93 (t, J=5 Hz, 2H), 4.7—5.2 (m, 2H), 5.4—6.1 (m, 1H). IR (neat): 3060, 1638, 1022, 994, 912 cm^{-1}; MS *m/e* (rel intensity): 166 (M^+, 0.9), 138 (11), 125 (11), 124 (11), 96 (24), 95 (23), 81 (50), 69 (80), 67 (93), 56 (97), 54 (87), 41 (100). Found: C, 86.92; H, 13.43 %. Calcd for $C_{12}H_{22}$: C, 86.66; H, 13.34%.

cis-*1-Allyl-2-hexylcyclopropane.* This compound was characterized by spectrometric data: PMR (CCl_4): δ −0.2—0.0 (m, 1H), 0.6—1.8 (m, 16H), 1.8—2.3 (m, 2H), 4.8—5.3 (m, 2H), 5.6—6.1 (m, 1H). IR (neat): 3060, 1640, 1024, 995, 913 cm^{-1}; MS *m/e* (rel intensity): 166 (M^+, 0.4), 96 (24), 95 (21), 81 (50), 67 (91), 55 (86), 54 (78), 41 (100).

trans-*1-Allyl-2-(benzyloxymethyl)cyclopropane (2e)*: Bp 80—85 °C (bath temp)/15 Torr; PMR (CCl_4): δ 0.2—1.1 (m, 4H), 2.00 (t, J=6 Hz, 2H), 3.2—3.4 (2H, $\underline{AB}$M), 4.43 (s, 2H), 4.8—5.4 (m, 2H), 5.5—6.2 (m, 1H), 7.23 (s, 5H); IR (neat): 3080, 1638, 1496, 1095, 1028, 996, 914, 740, 703 cm^{-1}; MS *m/e* (rel intensity): 202 (M^+, 0), 173 (1), 117 (7), 107 (8), 91 (100). Found: C, 82.98; H, 8.99%. Calcd for $C_{14}H_{18}O$: C, 83.17; H, 8.97%.

*7-*exo*-Allylnorcarane (2f)*: Bp 52—55 °C (bath temp)/18 Torr; PMR (CCl_4): δ 0.2—0.9 (m, 3H), 0.9—2.3 (m, 10H), 4.8—5.3 (m, 2H), 5.6—6.3 (m, 1H); IR (neat): 3080, 1635, 990, 910 cm^{-1}; MS *m/e* (rel intensity): 136 (M^+, 8), 121 (13), 107 (18), 95 (76), 79 (47), 67 (100). Found: C, 88.02; H, 11.99%. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84%.

7-endo-*Allyl-7*-exo-*methylnorcarane (3g).* To a THF (10 ml) solution of dibutylcopperlithium (5.0 mmol) at −48 °C was added **1g** (217 mg, 1.0 mmol) dissolved in THF (2 ml). After stirring at −48 °C for 30 min and at 0 °C for 30 min methyl iodide (1 ml) was added. Fifteen min thereafter the reaction was stopped by usual work-up. TLC purification (silica gel, hexane) gave **3g** (R_f 0.8—0.9, 145 mg, 96%). Bp 65—72 °C (bath temp)/22 Torr; PMR (CCl_4): δ 0.4—2.2 (m+s (δ 1.88), 15H), 4.5—6.0 (m, 3H); IR (neat): 3050, 1635, 995, 910 cm^{-1}. MS *m/e* (rel intensity): 150 (M^+, 0.9), 135 (13), 109 (96), 67 (100). Found: C, 87.95; H, 12.36%. Calcd for $C_{11}H_{18}$: C, 87.92; H, 12.08%.

7-exo-*Allyl-1-methylnorcarane (2h)*: Bp 70—75 °C (bath temp)/20 Torr; PMR (CCl_4): δ 0.2—0.7 (m, 2H), 0.7—2.3 (m+s (δ 1.03), 13H), 4.7—5.2 (m, 2H), 5.5—6.2 (m, 1H); IR (neat): 1635, 990, 905 cm^{-1}; MS *m/e* (rel intensity): 150 (M^+, 4), 121 (9), 109 (61), 96 (87), 81 (80), 67 (100). Found: C, 88.13; H, 12.20%. Calcd for $C_{11}H_{18}$: C, 87.92; H, 12.08%.

Methyl Cascarillate (10). A THF (2 ml) solution of **1d** (stereochemically pure) (208 mg, 1.0 mmol) was added to a THF (10 ml) solution of dibutylcopperlithium (5.0 mmol) at −48 °C. After stirring at −48 °C for 30 min and at 0 °C for 5 min methyl bromoacetate (1.5 ml) was added all at once, and the reaction mixture was allowed to warm to room temperature in 20 h. Preparative TLC (silica gel, hexane) of the crude product gave **10** (R_f 0.6—0.7, 151 mg, 75% yield). IR (neat): 3060, 1740, 1168, 1013 cm^{-1}; PMR (CDCl$_3$): δ 0.1—1.7 (m, 17H), 2.15 (d, J=6 Hz, 2H), 3.57 (s, 3H); MS *m/e*: 198 (M$^+$).

Alternative Synthesis of Methyl Cascarillate (10). To a well-stirred mixture of **2d** (and its cis isomer, 84: 16) (63 mg, 0.38 mmol), potassium carbonate (20 mg) in *t*-butyl alcohol (6 ml) and water (4 ml) was added an aqueous solution (10 ml) of sodium metaperiodate (550 mg) and potassium permanganate (20 mg). The resulting mixture was vigorously stirred for 3 h at room temperature, and then extracted with chloroform. Concentration of the chloroform extract gave an oil which was dissolved in ether (10 ml) and mixed with excess diazomethane ether solution. Usual work-up and purification (preparative TLC, silica gel, hexane–dichloromethane 3: 1, R_f 0.2—0.3) gave a mixture of **10** and its cis isomer (85: 15) (53 mg, 67% yield). Each product was separated by preparative GLC and compared with the authentic sample.[8)]

trans-*1-(1,1-Dimethyl-2-propenyl)-2-phenylcyclopropane (11) and* trans-*1-(3-methyl-2-butenyl)-2-phenylcyclopropane (12).* To dibutylcopperlithium (6.0 mmol) solution prepared as above was added **2a** (294 mg, 1.5 mmol) dissolved in THF (2 ml) at −48 °C. After 30 min 3-methyl-2-butenyl bromide (1 ml) was added and the reaction mixture was stirred for 30 min and worked up. Preparative TLC (silica gel, hexane, R_f 0.4—0.5) gave a mixture (7: 3) of **11** and **12** (269 mg, 97% yield). Each product was separated by preparative GLC (Apiezon L, 10% on Celite 545, 3 m, 180 °C). **11**: bp 55—60 °C (bath temp)/14 Torr; PMR (CCl$_4$): δ 0.6—1.5 (m+s (δ 1.03), 9H), 1.65 (t, J=6 Hz, 2H), 4.7—5.2 (m, 2H), 5.75 (dd, J=18, 10 Hz, 1H), 6.8—7.3 (m, 5H); IR (neat): 1635, 1605, 1004, 914 cm^{-1}; MS *m/e* (rel intensity): 186 (M$^+$, 3), 143 (9), 132 (21), 117 (72), 115 (44), 104 (100), 91 (72), 82 (88), 41 (78). Found: C, 90.19; H, 9.88%. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74%. **12**: bp 55—60 °C (bath temp) /14 Torr; PMR (CCl$_4$): δ 0.5—1.8 (m+2s (δ 1.60, 1.70), 11H), 2.07 (t, J=6 Hz, 2H), 5.17 (t, J=6 Hz, 1H), 6.7—7.3 (m, 5H); IR (neat): 1670, 1605, 1500, 1030 cm^{-1}; MS *m/e* (rel intensity): 186 (M$^+$, 4), 171 (3), 145 (21), 130 (27), 117 (100), 115 (39), 104 (40), 95 (38), 91 (48). Found: C, 90.23; H, 9.99%. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74%.

*1-Methyl-7-*exo*-octylnorcarane (4).* A THF (2 ml) solution of **1h** (152 mg, 0.80 mmol) was added dropwise at −48 °C to dibutylcopperlithium (5.0 mmol) in THF (10 ml). After stirring for 10 min at −48 °C and 2 h at 0 °C octyl bromide (1 ml) in HMPA (1 ml) was added to the reaction mixture which was stirred at 0 °C for 1 h and then worked up. As the crude product was contaminated with the recovered bromide, dodecane and hexadecane, the yield of **4** (50%) was estimated by GLC. Preparative GLC gave a pure sample to **4** completely identical with the authentic specimen. PMR (CCl$_4$): δ 0.2—0.4 (m, 2H), 0.7—2.1 (m+s (δ 1.01), 28H); IR (neat): 2920, 2850, 1463, 1370 cm^{-1}; MS *m/e* (rel intensity): 222 (M$^+$, 18), 123 (15), 109 (72), 96 (68), 81 (100), 67 (74), 55 (64).

Synthesis of Authentic Specimen of 4. Octylmagnesium bromide was prepared from octyl bromide (58 g, 0.30 mol) and magnesium (8.0 g, 0.33 mol) in ether (150 ml). The magnesium reagent was cooled to 0 °C and methacrylaldehyde (14.0 g, 0.20 mol) dissolved in ether (20 ml) was added dropwise over 30 min. After the addition was completed the reaction mixture was stirred at room temperature for 1 h, heated to reflux for 1 h, then cooled to room temperature and worked up. Distillation of the product at 83—84 °C/1.1 Torr gave **6** (35.0 g, 94% yield). PMR (CCl$_4$): δ 1.70 (s, 3H), 3.8—4.2 (m, 1H), 4.6—4.9 (m, 2H); IR (neat): 3350, 1660, 898 cm^{-1}. Found: C, 78.49; H, 13.36%. Calcd for $C_{12}O_{24}O$: C, 78.19; H, 13.13%.

A mixture of **6** (18.4 g, 0.10 mol), copper(I) chloride (4.95 g, 0.05 mol) and zinc powder (32.7 g, 0.50 mol) and ether (80 ml) was heated for 30 min, mixed with diiodomethane (67.0 g, 0.25 mol) and again heated to reflux overnight. Filtration and concentration gave a crude cyclopropylmethyl alcohol derivative which was added to 48% hydrobromic acid (100 ml) cooled at 0 °C in 3 min, and the mixture was vigorously stirred for 7 min. Extractive work-up with ether and distillation at 90—92 °C/0.06 Torr gave an unstable homoallyl bromide (5.65 g, 22% yield).

The homoallyl bromide dissolved in ethanol (6 ml) was added at 0 °C to diethyl sodiomalonate (prepared from diethyl malonate (4.80 g, 0.030 mol) and sodium ethoxide (0.030 mol) in ethanol (20 ml)). After stirring at 0 °C for 30 min and at reflux temperature for 4 h, the solvent was evaporated *in vacuo*. The residue was triturated with water and extracted with ether. Purification of the crude product gave **7** (3.27 g, 44% yield). Bp 130—133 °C/1 Torr. PMR (CCl$_4$): δ 0.7—2.2 (m+br s (δ 1.60), 30H), 3.0—3.2 (m, 1H), 4.13 (q, J=7 Hz, 4H), 5.10 (t, J=7 Hz, 1H); IR (neat): 1730, 1250, 1145, 1030 cm^{-1}. MS *m/e* (rel intensity): 295 (M$^+$−OEt, 11), 249 (14), 173 (100), 160 (93), 133 (43), 95 (45), 81 (88), 68 (84), 55 (70), 40 (59). Found: C, 70.50; H, 10.75%. Calcd for $C_{20}H_{36}O_4$: C, 70.54; H, 10.66%.

The malonate **7** (3.27 g) in 95% ethanol (13 ml) was mixed with potassium hydroxide (3.0 g) and heated at reflux temperature for 3 h, and then the solvent was evaporated *in vacuo*. To the residue was added acetic acid and the mixture was heated to reflux for 2 days. Work-up was performed by adding water, extracting with ether 4 times, washing the ethereal extracts with brine, drying the organic phase with sodium sulfate and by concentrating under reduced pressure. Distillation gave the corresponding monocarboxylic acid (1.47 g, 57%), bp 130—140 °C (bath temp)/0.03 Torr; PMR (CCl$_4$): δ 0.7—2.4 (m+s (δ 1.58), 26H), 5.10 (t, J=7 Hz), 11.7 (br s, 1H); IR (neat): 3600—2400, 1705 cm^{-1}. Found: C, 75.21; H, 12.01%. Calcd for $C_{15}H_{28}O_2$: C, 74.95; H, 11.74%.

Thionyl chloride (0.82 g, 6.9 mmol) was added to the carboxylic acid obtained as above and dissolved in benzene (8 ml), and the solution was heated to reflux for 1 h. Subsequent distillation gave the corresponding acid chloride (1.06 g, 74% yield). Bp 125 °C (bath temp)/0.05 Torr. The acid chloride was allowed to react with excess diazomethane ether solution at 0 °C overnight. Concentration *in vacuo* gave a crude diazo ketone **8** which was dissolved in cyclohexane (24 ml) and this solution was added over 1 h to the suspension of copper powder (110 mg) and copper(II) sulfate (7 mg) in cyclohexane (9 ml) heated at the reflux temperature. After 2 h the reaction mixture was cooled and filtered. Concentration of the filtrate and preparative TLC of the residue gave the norcaran-2-one derivative **9** (166 mg, 19% yield from the acid chloride). Bp 70—73 °C (bath temp)/1 Torr. IR (neat): 1678 cm^{-1}; MS *m/e*: 236 (M$^+$).

The ketone **9** (160 mg, 0.68 mmol) was mixed with 80% hydrazine hydrate (2.82 g, 45 mmol), hydrazine hydrochloride (577 mg, 5.5 mmol) and triethylene glycol (15.3 g). The mixture was heated at 130 °C for 2.5 h, mixed with potassium hydroxide (842 mg) and further heated at 210 °C for 2.5 h, while volatile compounds were distilled off. The residue and the distillate were mixed with water and extracted with ether. Concentration of the organic phase and subsequent preparative TLC gave **4** (82 mg, 54% yield). This compound was completely identical with the product obtained from **1h**. Bp 100—105 °C (bath temp)/13 Torr. Found: C, 86.18; H, 13.90%. Calcd for $C_{16}H_{30}$: C, 86.40; H, 13.60%.

*Thermal Decomposition of the Intermediate **13**.* To dibutylcopperlithium (4.0 mmol) in THF (10 ml) was added **1a** (193 mg, 1.0 mmol) dissolved in THF (2 ml) at −48 °C. The reaction mixture was stirred at −48 °C for 30 min and subsequently heated to reflux for 1 h. Usual work-up and preparative TLC (silica gel, hexane–ether 10:1, R_f 0.8) gave phenylcyclopropane (65 mg, 56%) characterized spectrometrically.

*Air Oxidation of the Intermediate **13**.* Dibutylcopperlithium (4.0 mmol) and **1a** (199 mg, 1.0 mmol) were mixed at −48 °C as above and after 30 min dry air was bubbled into the reaction mixture for 1 h. The initially black solution gradually turned to green, when the reaction mixture was quenched with methanol. Work-up and TLC analysis showed 7 UV sensitive products which were separated by preparative TLC. Three of them were characterized: *trans*-1-butyl-2-phenylcyclopropane (**14**)9) (R_f 0.5—0.65, 106 mg, 60%), *trans*-1-iodo-2-phenylcyclopropane (R_f 0.45, 21 mg, 12% yield) and 2,2′-diphenyl-1,1′-bicyclopropane (R_f 0.25, 9.2 mg, 8%). The last compound showed bp 110—115 °C (bath temp)/0.05 Torr; PMR (CCl_4): δ 0.6—1.9 (m, 8H), 6.7—7.3 (m, 10H); IR (neat): 3070, 3030, 3000, 1605, 1502, 1030, 905, 755, 700 cm^{-1}; MS *m/e* (rel intensity): 234 (M^+, 1.6), 180 (18), 143 (100), 128 (53), 115 (34), 91 (34). Found: C, 92.33; H, 7.79%. Calcd for $C_{18}H_{18}$: C, 92.26; H, 7.74%.

*Th Reaction of the Intermediate **13** with Methyl Propiolate.* To the intermediate **13** prepared by the standard procedure from **1a** (196 mg, 1.0 mmol) and dibutylcopperlithium (4.0 mmol) at −48 °C was added methyl propiolate (0.8 ml). The reaction mixture was stirred at −48 °C for 2 h, and then worked up. Preparative TLC (silica gel, hexane–ether 20:3) gave phenylcyclopropane (R_f 0.7—0.8, 17 mg, 14%) and methyl *trans*-3-(2-phenylcyclopropyl)acrylate (R_f 0.3—0.4, 93 mg, 46%) which showed bp 110—115 °C (bath temp)/2 Torr; PMR (CCl_4): δ 1.1—2.3 (m, 4H), 3.61 (s, 3H), 5.80 (d, J=16 Hz, 1H), 6.48 (dd, J=9, 16 Hz, 1H), 6.8—7.3 (m, 5H); IR (neat): 1710, 1638, 1605, 1503, 1250, 1142, 978, 753, 700 cm^{-1}; MS *m/e* (rel intensity): 202 (M^+, 9), 169 (13), 142 (98), 128 (84), 111 (100), 98 (71), 91 (35). Found: C, 77.44; H, 6.98%. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98%.

*The Reaction of the Intermediate **13** with Benzaldehyde.* Benzaldehyde (0.81 ml, 8.0 mmol) was added to the intermediate **13** prepared from **1a** (196 mg, 1.0 mmol) and dibutylcopperlithium (4.0 mmol). After 30 min the reaction mixture was worked up. Preparative TLC purification (silica gel, hexane–ether 3:1) gave phenylcyclopropane (R_f 0.7—0.8, 41 mg, 35%), and an adduct (R_f 0.1—0.2, 57 mg, 26%). The adduct was a mixture of two diastereomers, each isomer being separated by preparartive TLC (silica gel hexane–ether 1:1). The one of R_f 0.5—0.6 (11 mg) showed following properties: bp 140—145 °C (bath temp)/0.07 Torr; PMR (CCl_4): δ 0.6—1.6 (m, 3H), 1.6—2.1 (m, 1H), 2.20 (br s, 1H), 4.31 (d, J=6 Hz, 1H), 6.7—7.5 (m, 10H); IR (neat): 3350, 3060, 3030, 1605, 1500, 1031, 765, 700 cm^{-1}; MS *m/e* (rel intensity): 206 (M^+-H_2O, 12), 120 (100), 107 (33), 91 (38), 79 (35), 77 (25). Found: C, 85.95; H, 7.44%. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19%. The second diastereomer (R_f 0.4—0.5, 39 mg) gave bp 138—141 °C (bath temp)/0.05 Torr; PMR (CCl_4): δ 0.6—1.7 (m, 3H), 1.7—2.1 (m, 2H), 4.15 (d, J=7 Hz, 1H), 6.8—7.4 (m, 10H); IR (neat): 3350, 3040, 1603; 1505, 1018, 760, 700 cm^{-1}; MS *m/e* (rel intensity): 206 (M^+-H_2O, 25), 120 (100), 107 (38), 91 (44), 79 (38), 77 (31). Found: C, 85.83; H, 7.19%. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19%. Stereochemical assignment was not accomplished.

*Quenching the Intermediate **13** with Benzoyl Chloride.* Benzoyl chloride (0.93 ml, 8.0 mmol) was added to **13** prepared from **1a** (192 mg, 1.0 mmol) and dibutylcopperlithium (4.0 mmol) at −48 °C, and the mixture was stirred at −48 °C for 30 min. Usual work-up and preparative TLC (silica gel, hexane–ether 20:3, double development) gave 1-phenylbutanone (R_f 0.5—0.7, 802 mg, 5.0 mmol) and 1-benzoyl-2-phenylcyclopropane (R_f 0.4—0.5, 220 mg, 95% pure, 95% yield) which exhibited mp 43.5—44.0 °C; PMR (CCl_4): δ 1.2—1.6 (m, 1H), 1.6—2.0 (m, 1H), 2.3—2.9 (m, 1H), 7.03 (s, 5H), 7.2—7.5 (m, 3H), 7.6—8.1 (m, 2H); IR (Nujol): 3100, 1660, 1601, 1593, 1578, 1502, 1215, 1028, 985, 779, 766, 746, 700 cm^{-1}; MS *m/e*: 222 (M^+).

*Attempted Reaction of **13** with Vinyl Bromide.* Dibutylcopperlithium (6.0 mmol) prepared from copper(I) iodide (1.14 g, 6.0 mmol) and butyllithium (2.01 M hexane solution, 6.0 ml, 12 mmol) in THF (20 ml) was mixed with a THF (2 ml) solution of **1a** (299 mg, 1.5 mmol) at −48 °C. After 30 min vinyl bromide (1 ml) and 1 h thereafter HMPA (1 ml) were added, and the reaction mixture was allowed to warm to room temperature over 20 h. Work-up followed by preparative TLC (silica gel, hexane) gave **14** (R_f 0.6—0.65, 35 mg, 13%), 1-phenyl-2-vinylcyclopropane (R_f 0.4—0.5, 38 mg, 18%), and 2,2′-diphenyl-1,1′-bicyclopropane (R_f 0.2—0.3, 79 mg, 45%).

Alkylation of Bromobenzene with 3-Methyl-3-butenyl Bromide. Bromobenzene (158 mg, 1.0 mmol) dissolved in THF (2 ml) was added to dibutylcopperlithium (4.0 mmol) at −48 °C, and the mixture was stirred for 30 min at −48 °C, then warmed to 0°C, treated with 3-methyl-2-butenyl bromide (1 ml) and allowed to react for 40 min. Usual work-up followed by column chromatography on silica gel gave an oil (100 mg, 68%) consisted of **15** and **16**. The ratio (73:27) was estimated by PMR. **15** showed singlet at δ 1.37, vinylic absorption at δ 4.7—6.3, and **16** broad singlet at δ 1.70 and doublet at δ 3.23.

1-Allylnaphthalene. A Typical Procedure of Allylation of Bromoarenes. Under an argon atmosphere at −48 °C butyllithium (1.8 M hexane solution, 4.4 ml, 8.0 mmol) was added to THF (10 ml) suspension of copper(I) iodide (760 mg, 4.0 mmol). After 15 min 1-bromonaphthalene (200 mg, 0.97 mmol) was added, and the reaction mixture was warmed to 0 °C and stirred for 2 h until the bromide was all consumed. Then allyl bromide (970 mg) dissolved in HMPA (2 ml) and THF (3 ml) was added and the reaction mixture was stirred for 2 h. Work-up was effected by adding water (10 ml) and aq sat ammonium chloride (15 ml), filtering the mixture through Celite pad and by extracting with ether. The organic phase was dried (Na_2SO_4), concentrated and purified by column chromatography (silica gel, 75% yield). Bp 138—150 °C (bath temp)/27 Torr. PMR (CCl_4): δ 3.72 (d, J=6 Hz, 2H), 4.7—6.4 (m, 3H), 6.8—8.1 (m, 7H); IR (neat): 1595, 1506, 990, 910 cm^{-1}; MS *m/e*: 168 (M^+).

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