The mixture was then allowed to react at room temperature. The reaction mixture was treated with a solution of sodium thiosulfate. Treatment and isolation were carried out in a similar manner as above.

***anti*-*cis*-2-Oxatricyclo[6.3.0.0^{3,7}]undeca-4,10-diene (7a)**: ^{1}H NMR (CDCl$_3$, 400 MHz) δ 5.83–5.86 (m, 2 H), 5.74–5.77 (m, 2 H), 5.03–5.07 (m, 2 H), 2.62 (dm, J = 16.7 Hz, 2 H), 2.48–2.54 (m, 2 H), 2.33 (dm, J = 16.7 Hz, 2 H); ^{13}C NMR (CDCl$_3$, 22.5 MHz) δ 133.1 (d), 131.6 (d), 88.9 (d), 49.5 (d), 39.2 (t); IR (NaCl) 3070, 2950, 2920, 2860, 1450, 1360, 1110, 1070, 990, 890, 750, 700 cm^{-1}; GC-MS 148 (M$^+$). Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 80.32; H, 8.21.

***syn*-*cis*-2-Oxatricyclo[6.3.0.0^{3,7}]undeca-4,10-diene (7b)**: ^{1}H NMR (CDCl$_3$, 400 MHz) δ 5.81–5.84 (m, 2 H), 5.75–5.78 (m, 2 H), 5.08–5.10 (m, 2 H), 2.91–2.95 (m, 2 H), 2.36 (dm, J = 17.0 Hz, 2 H), 2.20 (dm, J = 17.0 Hz, 2 H); ^{13}C NMR (CDCl$_3$, 22.5 MHz) δ 133.8 (d), 131.8 (d), 89.9 (d), 44.3 (d), 34.1 (t); IR (NaCl) 3080, 2960, 2900, 2880, 1460, 1360, 1280, 1110, 1060, 1040, 1000, 970, 740, 720, 690 cm^{-1}; GC-MS 148 (M$^+$).

***anti*-10-Hydroxy-11-iodo-2-oxatricyclo[6.3.0.0^{3,7}]undec-4-ene (8)**: ^{1}H NMR (CDCl$_3$, 400 MHz) δ 5.91–5.94 (m, 1 H), 5.57–5.60 (m, 1 H), 5.38 (d, J = 6.6 Hz, 1 H), 4.55 (d, J = 4.0 Hz, 1 H), 4.35–4.39 (m, 1 H), 4.24 (s, 1 H), 3.53 (d, J = 9.3 Hz, 1 H), 2.83–2.88 (m, 1 H), 2.71–2.66 (m, 3 H), 2.30 (dm, J = 15.1 Hz, 1 H), 1.66 (dm, J = 9.0 Hz, 1 H); ^{13}C NMR (CDCl$_3$, 22.5 MHz) δ 134.8 (d), 129.5 (d), 90.7 (d), 90.6 (d), 82.4 (d), 50.5 (d), 47.5 (d), 40.0 (t), 39.8 (t), 34.0 (d); IR (KBr) 3450, 3070, 2950, 2870, 1630, 1440, 1360, 1050, 1000, 890 cm^{-1}; GC-MS 165 (M$^+$ – I). Anal. Calcd for $C_{10}H_{13}O_2I$: C, 41.12; H, 4.49. Found: C, 40.57; H, 4.55.

***anti*-10-Hydroxy-11-iodo-2-oxatricyclo[6.3.0.0^{3,7}]undec-4-ene (9)**: ^{1}H NMR (CDCl$_3$, 400 MHz) δ 5.88 (d, J = 5.6 Hz, 1 H), 5.64 (dd, J = 5.4, 2.2 Hz, 1 H), 5.25 (d, J = 5.4 Hz, 1 H), 4.66 (d, J = 6.1 Hz, 1 H), 4.48 (d, J = 4.2 Hz, 1 H), 3.73 (s, 1 H), 2.61–2.68 (m, 3 H), 2.30 (dm, J = 14.9 Hz, 1 H), 2.15 (s, 1 H), 2.03–2.13 (m, 1 H), 1.74–1.80 (m, 1 H); ^{13}C NMR (CDCl$_3$, 22.5 MHz) δ 134.2 (d), 130.4 (d), 90.6 (d), 89.6 (d), 72.8 (d), 48.4 (d), 48.1 (d), 45.1 (d), 39.7 (t), 39.4 (t); IR (NaCl) 3420, 3060, 2940, 2860, 1440, 1360, 1040, 890, 680 cm^{-1}; GC-MS 165 (M$^+$ – I).

1-Iodo-2-octanol (11): ^{1}H NMR (CDCl$_3$, 400 MHz) δ 3.49–3.54 (m, 1 H), 3.40 (dd, J = 10.0, 3.4 Hz, 1 H), 3.24 (dd, J = 10.0, 6.0 Hz, 1 H), 2.04 (d, J = 5.1 Hz, 1 H), 1.52–1.57 (m, 1 H), 1.37–1.26 (m, 9 H), 0.89 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (CDCl$_3$, 22.5 MHz) δ 70.9 (d), 36.6 (t), 31.7 (t), 29.1 (t), 25.6 (t), 22.6 (t), 16.4 (t), 14.1 (q); IR (NaCl) 3370, 2970, 2940, 2860, 1470, 1420, 1380, 1180, 1120, 1020 cm^{-1}; GC-MS 129 (M$^+$ – I).

***syn*-6-Deuterio-2-oxatricyclo[6.3.0.0^{3,7}]undeca-4,10-diene (13)**: ^{1}H NMR (CDCl$_3$, 400 MHz) δ 5.81–5.84 (m, 2 H), 5.75–5.78 (m, 2 H), 5.08 (s, 2 H), 2.91–2.95 (m, 2 H), 2.36 (dm, J = 17.0 Hz, 1 H), 2.20 (dm, J = 17.0 Hz, 2 H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 133.7 (d), 133.6 (d), 131.8 (d), 89.9 (d), 44.3 (d), 44.2 (d), 34.1 (t), [34.0, 33.8, 33.6]; IR (NaCl) 3070, 2950, 2860, 2150, 1450, 1360, 1100, 1070, 1000, 880, 730 cm^{-1}; GC-MS 149 (M$^+$).

Registry No. 1a, 1755-01-7; **1b**, 933-60-8; **6**, 10450-60-9; **7a**, 119297-94-8; **7b**, 119364-78-2; **8**, 119297-95-9; **10**, 111-66-0; **11**, 119297-96-0; **12**, 119297-97-1; **13**, 119297-98-2.

Carbanions. 24. Rearrangements of (*E*)- and (*Z*)-2,2-Diphenyl-3-pentenyl Alkali Metal Compounds[1]

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[(*E*)- and (*Z*)-2,2-diphenyl-3-pentenyl]lithium (**15** and **35**) were prepared by reaction of (*E*)- and (*Z*)-5-chloro-4,4-diphenyl-2-pentene, respectively, with lithium at –75 °C in diethyl ether or tetrahydrofuran (THF). These organolithium compounds when warmed in diethyl ether solution to 35 °C undergo [1,2]-sigmatropic rearrangement of the propenyl group with >95% retention of geometrical configuration of the *trans*-propenyl group and about 90% retention of configuration of the *cis*-propenyl group. The failure to incorporate an *n*-butyl group when **15** is warmed from –75 °C to 35 °C in the presence of an excess of *n*-butyllithium implies that these rearrangements are not likely to occur by elimination and then readdition of *cis*- or *trans*-propenyllithium. Instead an intramolecular syn-addition of the lithiomethyl group to the double bond of **15** or **35** followed by an anti-elimination in the intermediate cyclopropylcarbinyllithium (**33** or **36**) is proposed to account for the retention of configuration during propenyl migration (see Scheme V). A similar mechanism (Scheme VI) is suggested to account for retention of configuration during [1,2]-propenyl migration in the previously known Wittig rearrangements of benzyl propenyl ethers and methallyl propenyl ethers. In the solvent THF, rearrangement of **15** and **35** occurs on warming to 0 or 10 °C; however, here the *E* isomer **15** undergoes about a 50/50 ratio of [1,2]-phenyl to -propenyl migration. The *Z* isomer **35** similarly undergoes both phenyl and propenyl migration in THF but also undergoes evidently an intramolecular [1,5]-proton migration to give the allylic anion **42** (see Scheme VII). If **15** is treated with potassium *tert*-butoxide in THF at –75 °C, exclusive [1,2]-phenyl migration is observed. Possible interpretations of these cation and solvent effects are given.

While [1,2]-migrations of vinyl groups in organometallic compounds of magnesium and the alkali metals are well documented,[2-4] the stereochemistry of these rearrangements has been less well investigated. Rautenstrauch, Büchi, and Wüest[5] found that Wittig rearrangement of (*Z*)- and (*E*)-propenyl benzyl ethers brought about by *n*-butyllithium in an ethereal solution in the presence of tetramethylethylenediamine proceeded with retention of geometrical configuration of the migrating propenyl group. To account for the preservation of geometry of the migrating group, these workers proposed that the rear-

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[1] A brief account of a portion of this work was presented at the Symposium on Carbanions, 190th National American Chemical Society Meeting, Chicago, Sept 10, 1985; *Prepr. Am. Chem. Soc., Div. Pet. Chem.* **1985**, *30*, 597–603. More complete details of this work may be found in the following M.S. Theses completed at the Georgia Institute of Technology: D. L. Streeter (June, 1980), J. H. Northrop (June, 1981), R. L. Hughes (June, 1982), and K. W. Black (March, 1987).

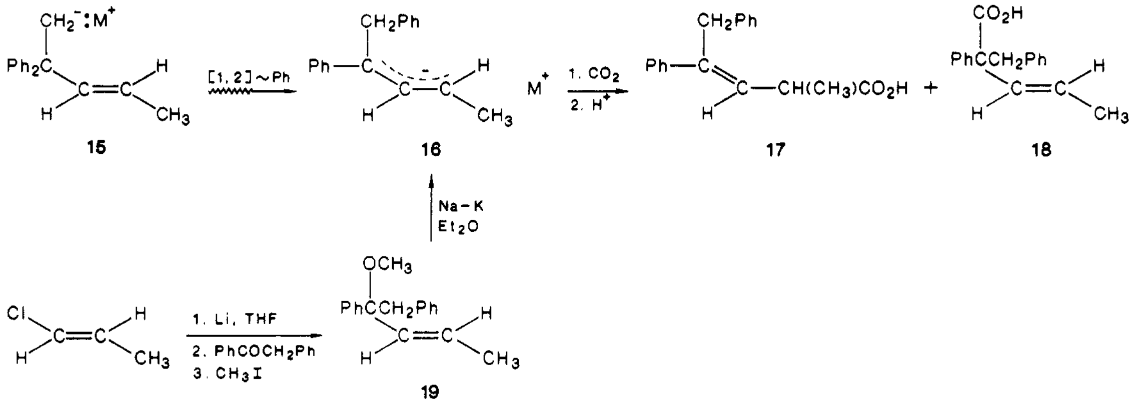
[2] Silver, M. S.; Shafer, P. R.; Norlander, J. E.; Rüchardt, C.; Roberts, J. D. *J. Am. Chem. Soc.* **1960**, *82*, 2646–2647. Patel, D. J.; Hamilton, C. L.; Roberts, J. D. *Ibid.* **1965**, *87*, 5144–5148. Howden, M. E. H.; Maercker, A.; Burden, J.; Roberts, J. D. *Ibid.* **1966**, *88*, 1732–1742. Maercker, A.; Roberts, J. D. *Ibid.* **1966**, *88*, 1742–1759.

[3] Hill, E. A. *J. Organomet. Chem.* **1975**, *91*, 123–271.

[4] Grovenstein, E., Jr. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 313–332.

[5] Rautenstrauch, V.; Büchi, G.; Wüest, H. *J. Am. Chem. Soc.* **1974**, *96*, 2576–2580.

Scheme I



rangement proceeded by initial cleavage into a carbonyl compound and a vinyllithium derivative, which then recombined (eq 1). Similar rearrangements of (*Z*)- and (*E*)-propenyl methallyl ethers also proceeded with retention of geometry of the migrating propenyl group.[5]

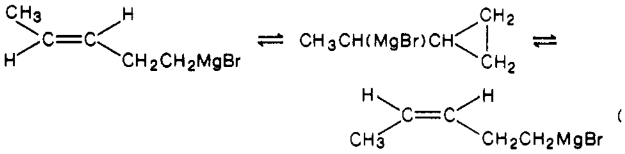
$$\mathrm{PhCHLiOCH{=}CHCH_3 \rightarrow [PhCHO + LiCH{=}CHCH_3] \rightarrow PhCH(OLi)CH{=}CHCH_3} \quad (1)$$

The somewhat related [1,5]-sigmatropic rearrangements of (*Z*)- and (*E*)-propenyl groups in cyclopentadienyl and indenyl alkoxides also proceed with stereospecific retention of geometry of the migrating propenyl group.[6] These, however, are believed to be concerted rearrangements, and alkyl, aryl, and cyclopropyl groups are also found to undergo [1,5]-sigmatropic shifts.[6]

In contrast Maercker and Streit[7] found that [1,2]-propenyl migration in 3-butenyl Grignard reagents, as revealed by deuterium labeling (eq 2), proceeded at a rate

$$\mathrm{CH_3CH{=}CHCH_2CD_2MgBr} \rightleftharpoons \mathrm{CH_3CH(MgBr)\overline{CHCD_2CH}_2} \rightleftharpoons \mathrm{CH_3CH{=}CHCD_2CH_2MgBr} \quad (2)$$

that was of "the same order of magnitude" as that of geometrical isomerization of the propenyl group (eq 3).



(3)

Also the irreversible [1,2]-propenyl rearrangement of [(*E*)-1-methyl-3-butenyl]magnesium bromide to (2-methyl-3-butenyl)magnesium[3] gave about a 1:1 mixture of *E* and *Z* isomers. These migrations of vinyl groups in Grignard reagents are regarded as proceeding by way of cyclopropylcarbinyl Grignard intermediates as shown in eq 2 and 3.[2-4,7] Hill[3] concluded that either intramolecular addition of the Grignard reagent to the double bond (and its reverse process) was not stereospecific or else inversion occurred at the new chiral center (the carbon linked to magnesium in the intermediate addition product) at a rate faster than ring opening.

The present work was undertaken to investigate the stereochemistry of [1,2]-propenyl migration in organoalkali metal compounds without heteroatoms. The organic group chosen for study was 2,2-diphenyl-3-pentenyl, which contains two phenyl groups that serve to stabilize the product of propenyl migration and ensure that rearrangement is irreversible.

Results

Preparation of (*Z*)- and (*E*)-5-Chloro-4,4-diphenyl-2-pentene (2 and 7). The cis chloride **2** was advantageously prepared by hydroboration[8] in tetrahydrofuran (THF) of the known[9] crystalline 5-chloro-4,4-diphenyl-2-pentyne (**1**) with bis(3-methyl-2-butyl)borane, followed by protonolysis[8] with acetic acid. This procedure gave 55% yield of pure crystalline (*Z*)-5-chloro-4,4-diphenyl-2-pentene (**2**). Alternatively **2** could also be obtained from chloromethylation of the carbanion **4** prepared by cleavage of (*Z*)-1,1-diphenyl-1-methoxy-2-butene (**3**) with Na–K in ether. (*E*)-5-Chloro-4,4-diphenyl-2-pentene (**7**) was prepared similarly by chloromethylation of the carbanion **6** from cleavage of (*E*)-1,1-diphenyl-1-methoxy-2-butene (**5**). In contrast to the (*Z*)-chloride, the (*E*)-chloride **7** was obtained as an oil, which resisted attempts of crystallization. This product by ^{1}H NMR analysis contained some 9% of the isomeric chloride 4-chloro-3-methyl-1,1-diphenyl-1-butene (**8**) from chloromethylation of the allylic anion **6** at the position adjacent to the methyl group.

Preparation of (*Z*)- and (*E*)-2,2-Diphenyl-4-hexenoic Acids (10a and 11a) and (*Z*)- and (*E*)-3,3-Diphenyl-4-hexenoic Acids (13a and 14a). These acids, which are the products expected from carbonation of the desired organoalkali metal reagents following and prior to propenyl rearrangement, respectively, were prepared from the known[9] 2,2-diphenyl-4-hexynoic acid (**9**) and 3,3-diphenyl-4-hexynoic acid (**12**). Hydroboration of the methyl esters of **9** and **12** with bis(3-methyl-2-butyl)borane followed by protonolysis[8] with acetic acid gave methyl (*Z*)-2,2-diphenyl-4-hexenoate (**10b**) and methyl (*Z*)-3,3-diphenyl-4-hexenoate (**13b**), respectively. Reduction of the acids **9** and **12** with sodium in liquid ammonia[10] gave the crystalline (*E*)-acids **11a** and **14a**, respectively. The structures of all of these acids and esters were confirmed by their spectral properties.

Preparation of Additional Reference Acids. Since reactions of the chlorides **2** and **7** with alkali metals gave, after carbonation, other carboxylic acids besides the expected nonrearranged acids (**13** and **14**) and the products of [1,2]-propenyl migration (**10** and **11**), other possible rearrangements of the organoalkali metal compounds had

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[6] Battye, P. J.; Jones, D. W. *J. Chem. Soc., Chem. Commun.* **1984**, 990–992.

[7] Maercker, A.; Streit, W. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 542–543; *Chem. Ber.* **1976**, *109*, 2064–2089.

[8] Brown, H. C. *Organic Syntheses via Boranes*; J. Wiley: New York, 1975; pp 18–21, 29–31, 38–40, 100–101.

[9] Grovenstein, E., Jr.; Chiu, K.-W.; Patil, B. B. *J. Am. Chem. Soc.* **1980**, *102*, 5848–5859.

[10] Cf. Henne, A. L.; Greenlee, K. W. *J. Am. Chem. Soc.* **1943**, *65*, 2020–2023.

Table I. Products from Reactions of (*Z*)- and (*E*)-5-Chloro-4,4-diphenyl-2-pentene with Lithium in Ethereal Solvents

					relative yields, %							
run	RCl	solvent (catalyst)	temp,[a] °C	time, h	10a	13a	11a	14a	17	18	32[b]	43
1	7	Et_2O	−75	2.5			4	87	3		6	
2	7	Et_2O	0	1.5			43	52	2		3	
3	7	Et_2O	35	3			90		7	3		
4	7	Et_2O	35	4			93		2	1	4	
5	7	THF	−75	2			3	79	1	6	10	
			−75	10			3	78	1	7	10	
			10	4			31		6	27	15	5[c]
6	7	THF	−75	3			3	75	2	10	9	
		(KO-*t*-Bu)	−75	1			4		15	69	12	
7	2	Et_2O	−75	4	12	84	1		3			
			35	4	83	1	9		6	1		
8	2	THF	−75	3	21	42	1	2	3	6		25
			0	4	28		1		5	18		38[d]

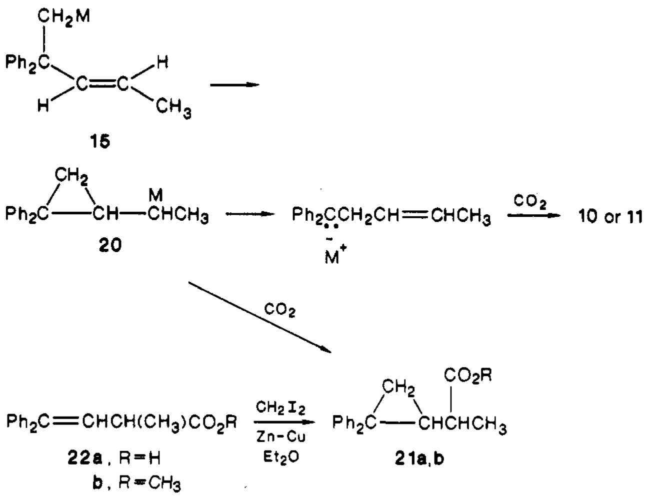
[a] The reactions with lithium were all carried out at −75 °C before the temperature was raised to the final value and time specified. [b] From isomeric chloride 8 present as an impurity in 7. [c] Also 15% of an isomeric ester (unknown A). [d] Also 10% of an isomeric ester (unknown B). See text for likely structures of unknowns.

to be considered. A likely possibility was [1,2]-phenyl migration since phenyl migration has been found to occur competitively with benzyl[11] and allyl[12] migration. The organoalkali compound (**15**) from the (*E*)-chloride **7** upon phenyl migration would be expected to give the least sterically encumbered anion **16** (cf. the reaction product[13] from (*E*)-1-phenyl-2-butene with KNH_2 in liquid ammonia at temperatures below −20 °C) as shown in Scheme I. For confirmation the anion **16** was independently prepared by cleavage of the methyl ester **19** (Scheme I) and characterized by carbonation to give the acids **17** and **18**. The trans geometrical configuration of **18** is confirmed by its ^1H NMR spectrum,[14] but the geometry of **17** (and hence of the corresponding bond in the carbanion **16**) is only provisional.

Since, as stated earlier, vinyl migration is believed by some workers to occur via addition of the organometallic group to the carbon–carbon double bond (cf. eq 2 and 3), the possibility exists that such adducts might be found in the present work. In other words, as shown in Scheme II, the organoalkali metal compound **15** may cyclize to **20** on the way to the product of propenyl migration. Some of **20** might survive, especially at low temperature, and if so could be detected on carbonation as the acid or methyl ester (**21a** or **21b**). To test this possibility the cyclopropane derivative **21b** was synthesized via the Simmons–Smith reaction.[15] This reaction gave **21b** as a mixture of the two possible diastereomers; however, neither of these was found in any of the products of carbonation from either **15** or its cis isomer.

Another possibility is that **15** cyclizes to (4-methyl-2,2-diphenylcyclobutyl)lithium (**23**) somewhat as in the presumed cyclization of 5-lithio-1-hexene to (2-methylcyclobutyl)carbinyllithium as intermediate leading to 5-lithio-3-methyl-1-pentene.[16] To check on the possible formation of **23**, the synthesis of its carbonation product **24a** as its ester, methyl *trans*-4-methyl-2,2-diphenylcyclobutanecarboxylate (**24b**), was effected via the photochemical reaction of 1,1-diphenylethene with methyl crotonate. This addition reaction was accompanied by the formation of comparable amounts of the isomer methyl *trans*-2-methyl-3,3-diphenylcyclobutanecarboxylate (**25b**) and small quantities of isomeric substances including what are thought to be the cis isomers of **24b** and **25b**. Gas chromatographic and mass spectral analyses, however, showed that *none* of the products from the photochemical synthesis were identical with any of the products obtained from reaction of (*Z*)- and (*E*)-5-chloro-4,4-diphenyl-2-pentene with alkali metals under the conditions of the present study.

Scheme II



Finally the chloride **8**, which was a minor impurity in the trans chloride **7**, would be expected to react with lithium to give the homoallylic organolithium compound **26a** (see Scheme III). The latter on the basis of the work of Maercker and Roberts[27] would be expected to cyclize

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[11] Grovenstein, E., Jr.; Williamson, R. E. *J. Am. Chem. Soc.* **1975**, *97*, 646–647.

[12] Grovenstein, E., Jr.; Cottingham, A. B. *J. Am. Chem. Soc.* **1977**, *99*, 1881–1889.

[13] Heiszwolf, G. J.; Van Drunen, J. A. A.; Kloosterziel, H. *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 1377–1390.

[14] Cf. Jackman, L. M.; Sternhell, S. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd ed.; Pergammon Press: Oxford, 1969; pp 301–304, 316–324.

[15] Smith, R. D.; Simmons, H. E. In *Organic Syntheses*; Baumgarten, H. E., Ed.; John Wiley and Sons: New York, 1973; Collect. Vol. V, pp 855–862.

[16] Richey, H. G., Jr.; Hill, E. A. *J. Org. Chem.* **1964**, *29*, 421–423.

[17] Maercker, A.; Roberts, J. D. *J. Am. Chem. Soc.* **1966**, *88*, 1742–1759.

[18] Grovenstein, E., Jr.; Cheng, Y.-M. *Chem. Commun.* 1970, 101–102. Grovenstein, E., Jr.; Cottingham, A. B.; Gelbaum, L. T. *J. Org. Chem.* **1978**, *43*, 4332.

[19] Walborsky, H. M.; Young, A. E. *J. Am. Chem. Soc.* **1964**, *86*, 3288–3296. Walborsky, H. M.; Aronoff, M. S. *J. Organomet. Chem.* **1973**, *51*, 31–53; **1973**, *51*, 55–75.

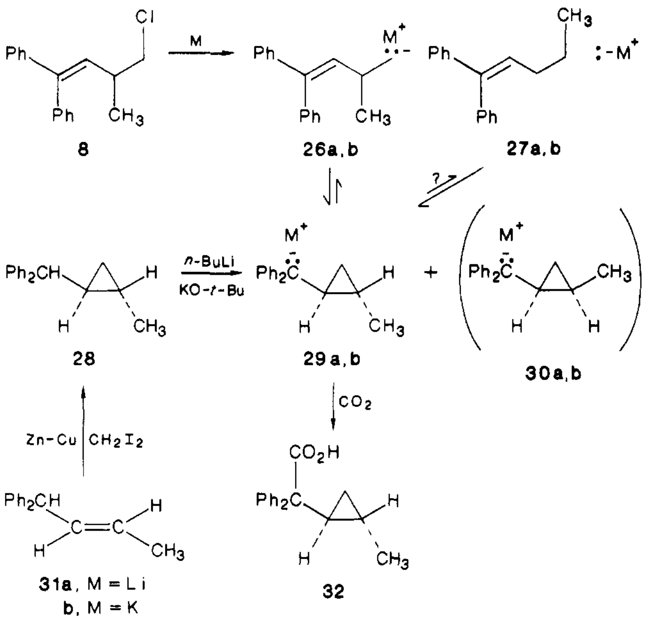
[20] Waack, R.; Doran, M. A. *J. Am. Chem. Soc.* **1969**, *91*, 2456–2461.

[21] Grovenstein, E., Jr.; Wentworth, G. *J. Am. Chem. Soc.* **1966**, *89*, 1852–1862.

[22] Whitesides, G. M.; Casey, C. P.; Krieger, J. K. *J. Am. Chem. Soc.* **1971**, *93*, 1379–1389.

[23] Amdur, I.; Hammes, G. G. *Chemical Kinetics: Principles and Selected Topics*; McGraw-Hill: New York, 1966; pp 63–64.

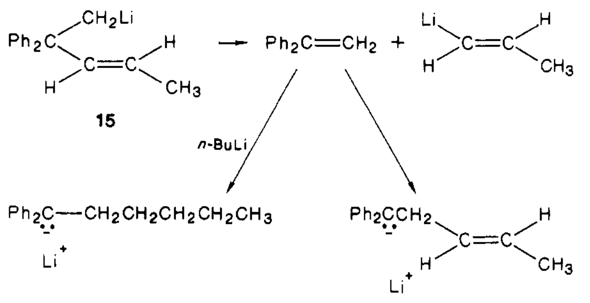
Scheme III



under some conditions to the corresponding cyclopropylcarbinyl isomer **29a**, which upon carbonation would yield the acid **32**. The acid **32** was independently synthesized (Scheme III) by metalation of the cyclopropane derivative **28** with *n*-butyllithium-potassium *tert*-butoxide to give **29b**, which was then carbonated. In the present work, according to the results of carbonation, both the potassium compound in THF and the lithium compound in diethyl ether at −75 °C exist primarily as the cyclopropylcarbinyl structure **29** rather than the homoallyl structure **26** (or **27**). In contrast Maercker and Roberts[17] found that the corresponding organoalkali metal compounds without the methyl substituent exist at 0 °C as the cyclopropylcarbinyl structure with potassium in diethyl ether or THF but as the open homoallyl structure with lithium in diethyl ether.

Reactions of (*Z*)- and (*E*)-5-Chloro-4,4-diphenyl-2-pentene (2 and 7) with Lithium. The relative yields of carboxylic acids from carbonation of the products from reaction of the cis and trans chlorides **2** and **7** with lithium in ethereal solvents are summarized in Table I. The major products at −75 °C were always the acids **13a** and **14a** of the same carbon skeleton as the starting chlorides. Lesser amounts of the products of phenyl migration (**17** and **18**) and of propenyl migration (**10a** and **11a**) were also formed. The yields of these byproducts appear to be poorly reproducible, 7–15% for the trans and 15–30% for the cis chloride, and the ratios of the byproducts are not in agreement with what is found during observable thermal rearrangement. Thus for the trans chloride **7** the ratio of propenyl to phenyl migration is 1:1 at −75 °C but 9:1 to 30:1 at 35 °C in diethyl ether; for the cis chloride **2** the ratio is 4:1 at −75 °C but 12:1 at 35 °C in diethyl ether. As has been previously suggested, skeletonal rearrangement at low temperature during the reaction of alkyl halides on the surface of metals likely occurs in intermediate free radicals[18] just as does configurational isomerism[19] in similar reactions of alkyl halides.

Scheme IV



Of greater interest is the rearrangement that occurs thermally upon warming the preformed organolithium reagents. The reagent from the trans chloride **7** in diethyl ether was partially converted to the product of [1,2]-propenyl migration after 1.5 h at 0 °C or completely converted after 3 h at 35 °C (save for the minor products of phenyl migration, which were evidently formed during preparation of the lithium reagent). Likewise the lithium reagent from the cis chloride **2** underwent essentially complete propenyl migration in diethyl ether at 35 °C. Whereas the propenyl migration of the trans compound occurred, as far as could be determined (>95%), with complete retention of geometry of the migrating propenyl group that of the cis compound occurred with about 10% (±5%) conversion of the *cis*-propenyl group into the *trans*-propenyl group.

These substantially complete retentions of geometry during propenyl migration are similar to those observed during Wittig ether rearrangements[5] and might occur by an elimination and readdition of propenyllithium as has been suggested for the Wittig rearrangement (see eq 1). To test this mechanism the initial organolithium reagent from the trans halide in diethyl ether was allowed to warm to 35 °C in presence of more than a 2-fold amount of *n*-butyllithium. Carbonation of the completely rearranged product, however, failed to reveal any addition of *n*-butyllithium to diphenylethylene as might have been expected for the elimination–readdition mechanism (see Scheme IV). Waack and Doran[20] have reported that in THF at 22 °C *n*-butyllithium is 2600–4000 times more reactive toward addition to 1,1-diphenylethylene than is vinyllithium at concentrations of 0.05–0.5 F in organolithium reagent. A qualitatively similar relative order of reactivity would be expected in the present work at 35 °C in diethyl ether. Hence the failure to detect any incorporation of *n*-butyllithium during the rearrangement of **15** disproves the formation of kinetically free propenyllithium and diphenylethylene as intermediates in the rearrangement of **15**. However, this experiment cannot disprove the intermediate formation of diphenylethylene and propenyl anion in a solvent cage and subsequent recombination of these species before diffusion can occur from the cage. In the related case of [1,2]-benzyl migration in (2,2,3-triphenylpropyl)lithium in THF it was possible to demonstrate the elimination–readdition of benzyllithium[21] by competitive addition of suitably reactive organolithium reagents to the intermediate diphenylethylene. Hence we regard the elimination–readdition of propenyllithium as a highly unlikely process for rearrangement of (2,2-diphenyl-3-propenyl)lithium (**15**).

The alternative rearrangement of **15** by fragmentation into diphenylethylene radical anion and *trans*-propenyl radical also seems unlikely because this involves promotion

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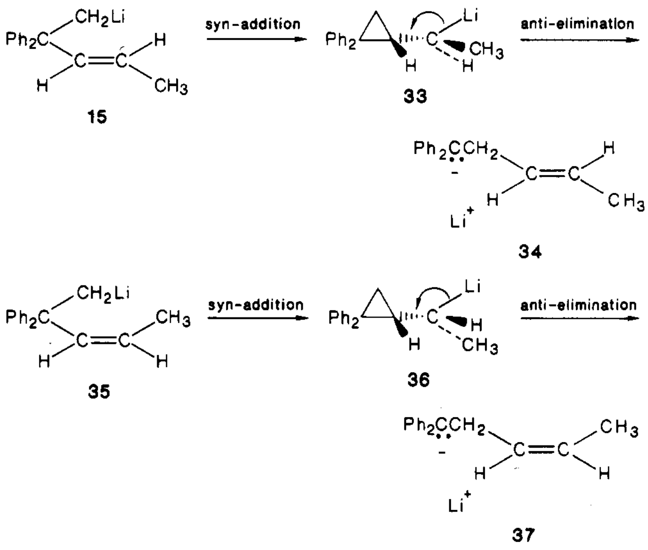
(24) Welch, J. G.; Magid, R. M. *J. Am. Chem. Soc.* **1967**, *89*, 5300–5301.

(25) Organolithium compounds are believed to be largely ionic in character. See: Streitwieser, A., Jr. *Acc. Chem. Res.* **1984**, *17*, 353–357. Streitwieser, A., Jr.; Williams, J. E., Jr.; Alexandratos, S.; McKelvey, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 4778–4784.

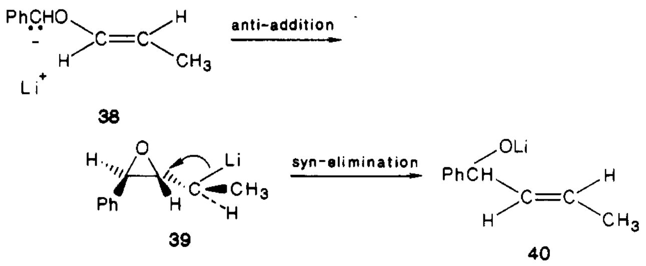
(26) Bach, R. D.; Badger, R. C.; Lang, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 2845–2848.

(27) Curtin, D. Y.; Koehl, W. J., Jr. *J. Am. Chem. Soc.* **1962**, *84*, 1967–1973. Witanowski, M.; Roberts, J. D. *J. Am. Chem. Soc.* **1966**, *88*, 737–741. Fraenkel, G.; Dix, D. T.; Carlson, M. *Tetrahedron Lett.* **1968**, 579–582.

Scheme V



Scheme VI



of an electron from a carbon–lithium bond into a high-lying antibonding molecular orbital of diphenylethylene and because this process would require that the *trans*-propenyl radical migrate at a rate of some 10^{11} s^{-1} in order to escape noticeable inversion of configuration, which has been estimated to occur with a rate constant of 10^9 s^{-1} ("probably a minimum value")[22] at 25 °C. Now if the propenyl radical can become reattached to its new position on the diphenylethylene radical anion at such a rate, near that of a bond vibration ($\sim 10^{13}$ s^{-1}),[23] its geometry would be maintained. We think, however, that such a high velocity is unreasonable for an ionic reaction, which proceeds with migration of the center of negative charge and likely requires considerable solvent (and/or cation) reorientation in the transition state.

A more likely hypothesis is that the propenyl group remains bound throughout its rearrangement and that rearrangement proceeds by an addition–elimination process via a cyclopropylcarbinyllithium as has been proposed for related rearrangements.[2-4,7] As Hill[3] has pointed out, however, such a rearrangement, which proceeds by a definite stereospecific course, say syn-addition (for which there is precedent[24] from an intermolecular reaction of an organolithium reagent in ether), would be expected to undergo syn-elimination and thus give a change in geometrical configuration of the migrating propenyl group, contrary to experimental observations in the present work.

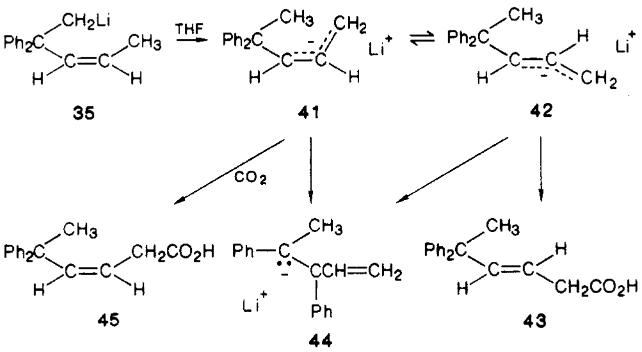
Nevertheless, the rule for similarity of stereochemical course of addition and elimination reactions is expected to hold only if other factors are equal. In the present case because of the location of two phenyl substituents on the cyclopropyl ring, the stereochemistry of the ring-opening reaction may reasonably be different from the stereochemistry of cyclization. Hence we propose the detailed mechanism of propenyl migration outlined in Scheme V (where only one enantiomer is drawn to illustrate the racemic compounds **33** and **36**). The rationale for syn-addition is that this geometry maintains the cation and anion in close juxtaposition from reactant to product (**15** to **33** and **35** to **36**) and so maximizes electrostatic stabilization of the tight ion pairs.[25] The explanation for anti-elimination in the present case is that the products of elimination, **34** and **37**, have a delocalized negative charge, a structural feature that implies looser ion pairing and greater stabilization of the ions by solvation. Since electrostatic attraction between cation and anion is thus weakened in the products **34** and **37**, it is also likely weakened in the transition states leading to these products. The advantage of the syn pathway is hence diminished so that the more usual anti-elimination mechanism prevails with its superior stabilization from orbital overlap[26] in the transition state.

Obviously Scheme V demands little interconversion of diastereomers **33** and **36** in order to achieve nearly complete retention of configuration during propenyl migration. Since organolithium compounds are essentially configurationally stable in pentane at −40 °C and undergo inversion at a rate of only some 10^2 s^{-1} at 25–30 °C in diethyl ether,[27] the requirement that the rate of ring opening of **33** and **36** exceeds the rate of interconversion of the diastereomers appears reasonable. Also the initially formed cyclopropylcarbinyllithium compounds need undergo only some 60° of rotation about the bond linking the cyclopropyl group to the carbinyl carbon atom to be in the optimum conformation for transformation into the products of anti-elimination. For diastereomer **36** from the cis lithium reagent (but not for **33**), this optimum conformation crowds the methyl group into the cis phenyl group; anti-elimination from the cis lithium compound is therefore retarded relative to that from the trans, and a little epimerization of **36** to **33** occurs prior to elimination.

Interestingly a mechanism similar to that of Scheme V can account for stereochemical retention during the Wittig ether rearrangement.[5] In the case of propenyl benzyl ethers, however, we would suggest that, following formation of the lithio derivative of the ether, the initial cyclization is by anti-addition while ring opening occurs by syn-elimination (see Scheme VI for the trans isomer). The reason for the differing stereochemistry of the initial and final steps is that the reactant **38** (unlike **15** or **35**) is expected to exist as a loose ion pair since the negative charge is delocalized and lithium ion is solvated by tetramethylethylenediamine while the product **40** exists as a tight ion pair (unlike **34** or **37**) since the negative charge is localized and strong electrostatic attraction binds lithium to oxygen. In other words Scheme VI is stereochemically similar to Scheme V operating in the reverse direction, i.e., **34** (or **37**) transforming into **15** (or **35**). However in the Wittig ether rearrangements, which have so far been studied[5] to ascertain the stereochemistry of propenyl migration, the product of cyclization (cf. **39**), in its formation and decomposition, can escape steric congestion by having the two large groups on the three-membered ring trans to one another. Hence the diastereomers from the *cis*- and *trans*-propenyl ethers both transform smoothly into the rearranged products with complete retention of configuration of the propenyl group.

As can be seen from Table I, the organolithium compound **15** can be formed from the trans chloride **7** as well in tetrahydrofuran (THF) as in diethyl ether. In THF, however, about as much phenyl migration as propenyl migration occurs on warming to 10 °C. A similar change in migratory aptitudes occurs with the cis chloride **2** on changing to solvent THF. Addition of potassium *tert*-

Scheme VII



butoxide to **15** at −75 °C results in almost complete phenyl migration (see Scheme I).

These results are in agreement with previous studies[28] upon competitive phenyl versus alkynyl migration in organoalkali metal compounds, wherein with lithium in THF solution at 0 °C only alkynyl migration occurred but with cesium at −75 °C exclusive phenyl migration took place. The results can be rationalized on the basis that alkynyl and propenyl migration occur via reaction intermediates (or transition states) with localized charge (cf. **33** and **36**), which require tight cation binding to increase their stability relative to the more delocalized anion and more loosely bound cation for phenyl migration. Hence increased solvation (THF vs diethyl ether) and larger cation (K^+ vs Li^+) favor phenyl over alkynyl or propenyl migration.

Looser ion pairing in THF implies a more reactive anion. Rearrangement occurs at a lower temperature in THF than in diethyl ether. Also especially for the cis halide **2** large amounts of another acid (**43**) from a new anion (**42**) appear in THF (see Scheme VII). The new anion evidently results from geometrical isomerization[29] of the cis anion **41**, which is expected from an intramolecular rearrangement of **35** (a [1,5]-proton migration[30]). The larger amount of **43** from the cis than from the trans chloride is in agreement with this mechanism. It should be noted that 10–15% of the carboxylic acids from the cis and trans chloride with lithium in THF remain unidentified. According to their mass spectral fragmentation patterns, unknown A is tentatively identified as the carbonation product of anion **44** (but formed from the trans chloride **7**) while unknown B likely is *cis*-5,5-diphenyl-3-hexenoic acid (**45**).[31]

Experimental Section[33]

Proton NMR spectra were determined at 60 MHz with a Varian, Model T-60A, NMR spectrometer or at 300 MHz with a Brucker, Model WM-300, NMR spectrometer. The ^{13}C NMR spectra were determined at 75 MHz with a Bruker, Model WM-300, NMR spectrometer. All NMR spectra are reported in parts per million (δ) downfield from tetramethylsilane as internal standard. Mass spectra were run on a Varian MAT 112S mass spectrometer interfaced to a Varian 3700 gas chromatograph and a Varian MAT SS200 data system. The columns used were fused-silica capillary columns coated with polydimethylsiloxane (SP-2100, 50 m × 0.2 mm), OV-1 (30 m × 0.25 mm), or polymethylphenylsiloxane (OV-17, 25 m × 0.1 mm). Routine analyses were performed on a Perkin-Elmer Model 881 gas chromatograph equipped with a hydrogen-flame ionization detector. The columns used were 6 ft × $^1/_8$ in., 3% SE 30 on 100–120 mesh Chromosorb W (AW DMCS); a 12 ft × $^1/_4$ in. 10% Carbowax 20-M on Chromosorb (AW DMCS); a 12 ft × $^1/_8$ in. 15% FFAP on 100–120 mesh Chromosorb W (AW DMCS). Later analyses were made on Varian 3600 and 1400 gas chromatographs equipped with flame ionization detectors and fused silica capillary columns (30 m × 0.25 mm, coated with SP-2100 or OV-1).

Quantitative and qualitative gas chromatographic analyses were made on methyl esters (prepared by reaction of the acids from carbonation with diazomethane) with use of an internal standard [biphenyl or 4,4′-bis(trimethylsilyl)biphenyl] and calibrations based on authentic samples. These analyses were confirmed by relative retention times on several columns, GC mass spectrometric fragmentation patterns, and NMR analyses, all in comparison with authentic samples. The relative retention times on the 15% FFAP column at 220 °C for the acids (as methyl esters) in this work are as follows: 1.79 (**32**), 1.88 (**11a**), 1.99 (**44**), 2.09 (**19**), 2.21 (**14a**), 2.22 (unknown A), 2.30 (**10a**), 2.70 (**13a**), and 3.14 (**17**) relative to the retention time of 4,4′-bis(trimethylsilyl)biphenyl (17.6 min).

All reactions with alkali metals were run under a nitrogen or, better, argon atmosphere with use of the usual Morton high-speed stirring apparatus,[34] which, for safety, was contained in a glovebox filled with nitrogen and/or carbon dioxide from the dry ice cooled bath. Diethyl ether and tetrahydrofuran (THF) were anhydrous grades and were freshly distilled from $LiAlH_4$ under an inert atmosphere directly into the Morton flask used for the organoalkali preparations.

(*Z*)-5-Chloro-4,4-diphenyl-2-pentene (2). A solution of 5-chloro-4,4-diphenyl-2-pentyne[9] (37.1 g, 146 mmol; mp 60.5–61.0 °C) in 100 mL of THF was added rapidly by cannula with stirring to excess bis(3-methyl-2-butyl)borane[8] (292 mmol) in 600 mL of THF at −5 °C under a nitrogen atmosphere. The reaction mixture was allowed to warm to room temperature and then stand for 72 h under a nitrogen atmosphere. Glacial acetic acid (75 mL) was slowly added to the reaction mixture, which was then allowed to react for 100 h with constant stirring before the reaction mixture was poured into ice water. The product was extracted with four 150-mL portions of diethyl ether, and the ethereal extract was treated with 50 mL of 3 N NaOH followed by dropwise addition of 33 mL of 30% H_2O_2 over a 15-min period followed by constant stirring for 1 h. The ether layer was separated and washed with a saturated NaCl solution and then dried over anhydrous $MgSO_4$ before removal of volatile components on a rotatory evaporator. Since an ^1H NMR analysis of the product indicated that some of a boron byproduct remained, the product was taken up again in ether, and the oxidation with alkaline hydrogen peroxide was repeated with the same quantities of reagents as previously used. The crude product amounted to 46 g, and after recrystallization from *n*-pentane at 0 °C gave 20.5 (55% yield) of white crystalline **2**: mp 36.5–37.5 °C; ^1H NMR (300 MHz in CCl_4) δ 1.03 (d of d, J = 1.8 Hz, 7.2 Hz, 3 H, CH_3), 4.13 (s, 2 H, CH_2Cl), 5.76 (d of q, J = 7.2 Hz, 11.8 Hz, 1 H, $CH{=}CHCH_3$), 6.12 (d of q, J = 1.8 Hz, 11.8 Hz, 1 H, $CH{=}CHCH_3$), 7.15–7.29 (m, 10 H, Ar*H*); IR ($CDCl_3$) 3090 (m), 3070 (s), 3030 (s), 2980 (m), 2950 (m), 2930 (m), 2440 (m), 2420 (s), 1650 (w), 1605 (m), 1520 (m), 1500 (s), 1480 (m), 1450 (s), 1440 (m), 1400 (m), 1360 (m), 1340 (m), 1280 (m), 1220 (s), 1080 (m), 1040 (s), 950 (s), 880 (m), 850 (m), 750 (s), 675 (s), 630 (s). Anal. Calcd for $C_{17}H_{17}Cl$: C, 79.52; H, 6.67; Cl, 13.81. Found: C, 79.50; H, 6.69; Cl, 13.81.

In an alternative synthesis 10.89 g (45.7 mmol) of (*Z*)-1,1-diphenyl-1-methoxy-2-butene (**3**) in 70 mL of diethyl ether was added slowly over a period of 25 min to eutectic Na-K alloy (6.77 g of K, 1.91 g of Na) finely dispersed in 250 mL of anhydrous ether

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[28] Grovenstein, E., Jr.; Chiu, K.-W.; Patil, B. B. *J. Am. Chem. Soc.* **1980**, *102*, 5848–5859.

[29] Cf. the low rotational barrier for allyllithium: Thompson, T. B.; Ford, W. T. *J. Am. Chem. Soc.* **1979**, *101*, 5459.

[30] Maecker, A.; Eckers, M.; Posslack, M. *J. Organomet. Chem.* **1980**, *186*, 193–203. Wroczynski, R. J.; Baum, M. W.; Kost, D.; Mislow, K.; Vick, S. C.; Seyferth, D. *J. Organomet. Chem.* **1979**, *170*, C29–C33. Cf. Yates, B. F.; Random, L. *J. Am. Chem. Soc.* **1987**, *109*, 2910–2915.

[31] Note that 4,4,4-triphenyl-2-butenylpotassium has recently been found[32] to undergo [1,2]-phenyl migration to 1,1,2-triphenyl-3-butenylpotassium. More surprisingly, 4,4,4-triphenyl-2-butenylpotassium under conditions of torsional equilibrium contains about a 1:1 ratio of cis/trans stereoisomers at −50 °C in THF solution.

[32] Moret, E.; Fürrer, J.; Schlosser, M. *Tetrahedron* **1988**, *44*, 3539–3550. We are greatly indebted to Professor Schlosser for informing us of these results prior to publication.

[33] All melting points are corrected while boiling points are uncorrected. Elemental analyses are by Atlantic Microlab, Inc., Atlanta, GA. See supplementary material for additional experimental details.

[34] Morton, A. A.; Redman, L. S. *Ind. Eng. Chem.* **1948**, *40*, 1190.

at gentle refluxing temperature under a nitrogen atmosphere. This rection was run in a 500-mL creased Morton flask equipped with a high-speed stirrer,[34] a condenser, a pressure-equalizing dropping funnel, and a glass-siphon system, which led from the bottom of the Morton flask out through a stopcock. The reaction is markedly exothermic as noted by the increased reflux rate in the condenser. A 6-mL aliquot was removed from the deep red solution and decomposed with ethanol; the ^{1}H NMR spectrum of the product (after removal of solvent) showed complete disappearance of the OCH_3 singlet at δ 3.07. Mercury (10 mL) was added dropwise to the reaction mixture to amalgamate any unreacted Na–K alloy. The red solution of carbanion was siphoned into a 1000-mL round-bottomed flask containing 125 mL of CH_2Cl_2 and 125 mL of diethyl ether cooled to –40 °C and stirred with a magnetic stirrer under a nitrogen atmosphere. All residual carbanion was washed from the reaction flask into the CH_2Cl_2 solution by two 200-mL portions of anhydrous ether. The reaction mixture was then allowed to warm to room temperature; the red color disappeared during warm up. The ethereal solution was washed well with nearly saturated NaCl solution and dried over anhydrous $MgSO_4$. Removal of all solvent, finally with a vacuum pump at 80 °C, gave 9.2 g of crude product containing 76% of **2** by ^{1}H NMR analysis or 60% yield. Recrystallization from *n*-pentane gave pure white crystals (3.9 g, 33% yield) identical with those from the previous synthesis.

(*Z*)-1,1-Diphenyl-1-methoxy-2-butene (3). Propenyllithium was prepared from 1-bromopropene (45.7 g, 378 mmol; about 80% cis isomer by ^{1}H NMR analysis) and lithium sand (11.2 g, 1.6 g-atoms, containing 1% Na) by the general procedure of Whitesides and co-workers[22,35] except that the reaction was run in 450 mL of THF at –75 °C for 6 h. A Watson–Eastham titration[36] indicated that 202 mmol of propenyllithium had been formed. To this cold solution under nitrogen with stirring was added benzophenone (34.9 g, 192 mmoles) in 100 mL of THF, and the solution was allowed to warm to 0 °C whereupon methyl iodide (42 mL, 0.67 mol) was added dropwise with cooling over a 15-min period. Stirring was stopped, and the solution was then held at gentle reflux for 2 h, whereupon more methyl iodide (45 mL) was added and reflux was continued for 12 more hours. At this time an ^{1}H NMR analysis of a small aliquot indicated that the number of CH_3O protons was equal to the number of CH_3 protons of the propenyl group of the adduct. The reaction solution was filtered under nitrogen to remove unreacted lithium residues. (*Caution*! Finely divided lithium is pyrophoric.) The solvent was removed on a rotatory evaporator, and the crude product was taken up in ether and washed with aqueous NaCl, and the ethereal solution was dried over anhydrous $MgSO_4$. The solvent was removed in vacuo finally at 80 °C to give 47 g of crude product. Recrystallization from *n*-pentane gave 13 g of white crystalline **3**: mp 57.5–58.5 °C; ^{1}H NMR (300 MHz in $CDCl_3$) δ 1.49 (d of d, J = 1.8 Hz, 7.1 Hz, 3 H, CH_3), 3.14 (s, 3 H, OCH_3), 5.86 (d of q, J = 7.1 Hz, 11.5 Hz, 1 H, $CHCHCH_3$), 6.16 (d of q, J = 1.8 Hz, 11.5 Hz, 1 H, $CH{=}CHCH_3$), 7.1–7.5 (m, 10 H, ArH); IR (CCl_4) 3100 (m), 3075 (s), 3045 (s), 2960 (s), 2840 (s), 1652 (m), 1602 (m), 1495 (s), 1455 (s), 1253 (s), 1180 (s), 1080 (s), 870 (s), 705 (s), 675 (m) cm^{-1}. Anal. Calcd for $C_{17}H_{18}O$: C, 85.76; H, 7.61. Found: C, 85.58; H, 7.62.

(*E*)-1,1-Diphenyl-1-methoxy-2-butene (5). (*E*)-1-Propenyllithium was prepared from 20.98 g (274 mmol) of 1-chloro-1-propene (>96% trans isomer by ^{1}H NMR analysis) and lithium sand (8.88 g, 1.3 g-atoms, containing 1% Na) by the general procedure of Whitesides and co-workers[22,35] except that the reaction was run in 250 mL of THF at –60 °C for 8 h. A Watson–Eastham titration[36] at this time indicated that 170 mmol of propenyllithium had been formed. The temperature of the reaction mixture was lowered to –75 °C, and then benzophenone (30.0 g, 164 mol) in 100 mL of THF was added. The reaction mixture was allowed to warm to 0 °C and then, to remove much unreacted lithium, was transferred via cannula under nitrogen to a round-bottomed flask with aid of 300 mL of THF to rinse out the reaction vessel. The mixture was kept at 0 °C with stirring while excess methyl iodide (64 mL, 1.03 mol) was added. After the initial vigorous reaction subsided, the reaction mixture was kept at reflux temperature for 36 h before workup as for the *Z* isomer **3**. The yield of crude product amounted to 39 g, which after recrystallization from *n*-pentane gave 23 g (58% yield) of white crystalline **5**: mp 53.5–54.5 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.69 (d of d, J = 1.7 Hz, 6.6 Hz, 3 H, CH_3), 3.07 (s, 3 H, OCH_3), 5.41 (d of q, J = 6.6 H, 15.5 Hz, 1 H, $CH{=}CHCH_3$), 6.04 (d of q, J = 1.7 Hz, 15.5 Hz, 1 H, $CH{=}CHCH_3$), 7.1–7.3 (m, 10 H, ArH); IR (CCl_4) 3090 (m), 3063 (m), 3035 (m), 2943 (m), 2920 (m), 2830 (m), 1491 (m), 1448 (s), 1075 (s), 980 (s), 728 (s), 705 (s) cm^{-1}. Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.47; H, 7.67.

(*E*)-5-Chloro-4,4-diphenyl-2-pentene (7). This compound was prepared starting with cleavage of the trans ether **5** (22.0 g, 0.092 mol) with 15.2 g of eutectic Na–K alloy in diethyl ether followed by reaction of the resulting carbanion **6** with excess of CH_2Cl_2 (1.1 mol) by the procedure used for preparation of the cis chloride **2** from the cis ether **3**. The yield of crude chloride was 21.2 g. This product after two distillations through a Hickman molecular still at a bath temperature of 110–140 °C at 0.25 Torr amounted to 17.3 g of colorless oil, which resisted attempts at crystallization. This product was used in reactions with alkali metals. The analytical sample was subjected to four more distillations through the Hickman still. An ^{1}H NMR analysis ($CDCl_3$) at 300 MHz indicated that the product was **7** containing about 9% of isomeric **8**: ^{1}H NMR for **7** at δ 1.74 (d of d, J = 1.7 Hz, 6.4 Hz, 3 H, CH_3), 4.20 (s, 2 H, CH_2Cl), 5.20 (d of q, J = 6.4 Hz, 15.6 Hz, 1 H, $CH{=}CHCH_3$), 6.15 (d of q, J = 1.7 Hz, 15.6 Hz, 1 H, $CH{=}CHCH_3$), 7.1–7.3 (m, 10 H, ArH); ^{1}H NMR for **8** δ 1.06 (d, J = 6.6 Hz, 3 H, CH_3), 2.69 (m, 1 H, $CHCH(CH_3)CH_2Cl$), 3.37 (m, 2 H, $CH(CH_3)CH_2Cl$), 5.90 (d, J = 9.9 Hz, 1 H, $C{=}CH$-$(CH_3)CH_2Cl$), ArH hidden by ArH of **7**. The assignments of the nonaromatic protons in **8** were confirmed by spin decoupling the proton at δ 2.69. Anal. Calcd for $C_{17}H_{17}Cl$: C, 79.52; H, 6.67; Cl, 13.81. Found: C, 79.52; H, 6.72; Cl, 13.61.

Methyl (*Z*)-2,2-Diphenyl-4-hexenoate (10b). A solution of 2.87 g (10.3 mmol) of methyl 2,2-diphenyl-4-hexynoate (made by reaction of CH_2N_2 with the known acid[9] **9**) in 20 mL of anhydrous THF was added to 22 mL of a THF solution of bis(3-methyl-2-butyl)borane[8] (11.3 mmol) at –5 °C under a nitrogen atmosphere. The solution was allowed to warm and then kept at room temperature for 72 h before addition of glacial acetic acid (10 mL). The solution was stirred for 120 h at room temperature and then for 4 h at 100 °C before being poured into ice water. The product was extracted with ether, and the ethereal solution was treated at room temperature with 10 mL of 3 N NaOH followed by dropwise addition of 8 mL of 30% H_2O_2 and stirring for 45 min. The ethereal extract was distilled finally in a Hickman still at 0.7 mm and 180 °C (bath) to give 0.32 g of methyl ester (**10b**). Attempts to crystallize this product from *n*-pentane gave crystals, which melted on the sintered-glass filter: ^{1}H NMR (60 MHz, CCl_4) δ 1.31 (br d, J = 5 Hz, 3 H, $CHCH_3$), 3.08 (br d, J = 5 Hz, 2 H, CH_2CH), 3.52 (s, 3 H, OCH_3), 5.26 (m, 2 H, $CH{=}CH$), 7.15 (br s, 10 H, ArH); MS M$^+$ calcd for $C_{19}H_{20}O_2$ *m/e* 280.1463, found 280.1448; *m/e* (relative intensity) 280 (0.5), 226 (18), 225 (100), 221 (4), 197 (54), 166 (20), 165 (70), 143 (9), 129 (12), 128 (9), 115 (10), 105 (35), 91 (33).

(*E*)-2,2-Diphenyl-4-hexenoic Acid (11a). To 100 mL of liquid ammonia (distilled from a dark blue solution containing sodium metal) was added 0.360 g (15.7 mg-atoms) of sodium metal, and the solution was stirred at –78 °C under a nitrogen atmosphere until solution was complete. An ethereal solution of 2,2-diphenyl-4-hexynoic acid (1.09 g, 4.1 mmol) was added dropwise over a 5-min period. The solution was allowed to warm to its boiling point and was held at reflux temperature for 2 h before decomposition of the excess sodium with ammonium sulfate. The crude acidic product was isolated by the usual extraction procedures and amounted to 0.86 g (79% yield) of crude **11a**. After recrystallization from *n*-pentane and then aqueous ethanol, 0.43 g of pure white crystals was obtained: mp 118.5–119.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.48 (d, J = 4.5 Hz, 3 H, $CH{=}CHCH_3$), 3.07 (d, J = 5.3 Hz, 2 H, $CH_2CH{=}CH$), 5.23 (m, 2 H, $CH{=}CHCH_3$), 7.3 (m, 10 H, ArH); IR ($CHCl_3$) 1705 (s), 970 (m). Anal.

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Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 80.89; H, 6.82. MS M^+ calcd for methyl ester (**11b**), $C_{19}H_{20}O_2$, *m/e* 280.1463, found 280.1455; *m/e* (relative intensity) 225 (100), 197 (64), 166 (18), 165 (42), 143 (9), 128 (10), 115 (10), 105 (41), 91 (31).

Methyl (*Z*)-3,3-Diphenyl-4-hexenoate (13b). This compound was prepared from 1.52 g (5.4 mmol) of methyl 3,3-diphenyl-4-hexynoate (prepared by reaction of diazomethane with the known acid[9] **12**) by the same procedure used for the preparation of **10** from **9**. The pure product was collected as crystals from the condenser of a Hickman still after distillation at 1 mm. The pure white crystals of **13b** (0.60 g, 40% yield) had mp 71.0–72.0 °C: ^1H NMR (60 MHz, CCl_4) δ 1.03 (d of d, J = 7 Hz, 1.8 Hz, 3 H, $CHCH_3$), 3.22 (s, 2 H, $CH_2CO_2CH_3$), 3.34 (s, 3 H, OCH_3), 5.66 (d of q, J = 11.5 Hz, 7.0 Hz, 1 H, $CH{=}CHCH_3$), 6.36 (d of q, J = 11.5 Hz, 1.8 Hz, 1 H, $CH{=}CHCH_3$), 7.16 (br s, 10 H, Ar*H*); IR ($CHCl_3$) 1645 (w), 1405 (m), 700 (s) cm^{-1}; MS M^+ calcd for $C_{19}H_{20}O_2$ *m/e* 280.1463, found 280.1376; *m/e* (relative intensity) 280 (3), 248 (2), 220 (9), 208 (9), 207 (52), 206 (52), 205 (15), 192 (8), 191 (19), 189 (6), 178 (15), 165 (14), 129 (100), 128 (26), 117 (6), 115 (15), 105 (4), 91 (57). Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19. Found: C, 80.93; H, 7.06.

(*E*)-3,3-Diphenyl-4-hexenoic Acid (14a). This compound was prepared from 0.91 g (3.4 mmol) of 3,3-diphenyl-4-hexynoic acid (**12**) by the same procedure used for preparation of **11a** from **9**. The crude product after recrystallization from aqueous ethanol amounted to 0.77 g (85% yield) of white crystals: mp 167.0–168.0 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 1.71 (d of d, J = 6.5 and 1.6 Hz, 3 H, $CH{=}CHCH_3$), 3.31 (s, 2 H, CH_2CO_2H), 5.01 (d of q, J = 15.6 and 6.5 Hz, 1 H, $CH{=}CHCH_3$), 6.35 (d of q, J = 15.6 and 1.6 Hz, 1 H, $CH{=}CHCH_3$), 7.2 (m, 10 H, Ar*H*); IR ($CHCl_3$) 1600 (w), 985 (m). Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 80.81; H, 6.81; MS M^+ calcd for methyl ester **14b** ($C_{19}H_{20}O_2$) *m/e* 280.1463, found 280.1471; *m/e* (relative intensity) 280 (5), 248 (2), 220 (10), 208 (9), 207 (55), 206 (51), 205 (17), 191 (19), 179 (9), 178 (16), 165 (13), 143 (9), 129 (100), 128 (25), 127 (8), 115 (15), 105 (13), 103 (11), 91 (54).

(*E*)-4,5-Diphenyl-2-methyl-3-pentenoic Acid (17) and (*E*)-2-Benzyl-2-phenyl-3-pentenoic Acid (18). (*E*)-1-Propenyllithium was prepared from (*E*)-1-chloropropene (26.5 g, 0.346 mol) and excess lithium sand (8.7 g, 1.25 mol) in 225 mL of THF as described earlier. After titration indicated that propenyllithium formation was 78% complete, deoxybenzoin (44.4 g, 0.226 mol) in 100 mL of THF was added slowly to the solution at -50 °C with stirring, and then the solution was allowed to warm to 25 °C. The solution was transferred under nitrogen via cannula (to remove most of the excess lithium) to a second flask, 62 mL (1.00 mol) of methyl iodide was added, and the solution was held at reflux for 72 h. The reaction mixture yielded 56 g of crude product, which by ^1H NMR analysis contained some 70% of the desired ether (**19**). Dissolution of the product in *n*-pentane and chilling yielded 6 g of *trans*-stilbene (^1H NMR, MP, MS). A 24.6-g portion of the crude ether **19** (after removal of the pentane) was dissolved in 30 mL of diethyl ether and added dropwise over 35 min to 15.9 g (0.32 mol of K) of eutectic Na–K alloy stirred vigorously at reflux in a Morton flask. While there was an instantaneous brown-red color on first addition of **19**, the reaction suddenly became highly exothermic 20 min after completion of the addition with the result that about half of the reaction mixture was pushed past the condenser into the nitrogen line and lost. Mercury (10 mL) was added dropwise with stirring to amalgamate the excess Na–K, and the reaction mixture was forced onto solid carbon dioxide. The usual acid–base extraction procedure gave 7.3 g (28% yield) of carboxylic acids, which by NMR analysis of the methyl esters consisted of a 3:2 ratio of **18**:**17**. The ^1H NMR spectrum (60 MHz, CCl_4) of this mixture of methyl esters allows the following spectral assignments: for **18**, δ 1.75 (d of d, J = 1 Hz, 6 Hz, $CH_3CH{=}CH$), 3.38 (s, CH_2Ph), 5.36 (d of q, J = 6 Hz, 16 Hz, $CH_3CH{=}CH$), 5.89 (d of q, J = 1 Hz, 16 Hz, $CH_3CH{=}CH$); for **17**, δ 1.28 (d, J = 7 Hz, $CHCH_3$), 3.90 (s, CH_2Ph), 5.94 (d, J = 10 Hz, $C{=}CHCH$); for both **17** and **18**, δ 3.56 (s, OCH_3), 7.1 (m, Ar*H*). The failure to observe allylic coupling of the vinylic and benzylic hydrogens of **17** argues for their *transoid* relation as shown in structure **17** of Scheme I; the large value of the vinylic coupling in **18** confirms the trans arrangement of the olefinic protons.[14] The GC–MS of **17** gave *m/e* (relative intensity) 280 (46), 221 (17), 220 (10), 205 (11), 193 (44), 192 (11), 189 (6), 178 (13), 165 (6), 143 (49), 131 (13), 129 (37), 128 (29), 115 (49), 105 (18), 91 (100); for **18** 280 (3), 248 (4), 189 (20), 157 (19), 129 (100), 128 (16), 115 (11), 91 (28).

Reactions of (*Z*)- and (*E*)-5-Chloro-4,4-diphenyl-2-pentene with Lithium. In a typical experiment (run 1, see Table I) lithium sand was prepared from 3.7 g (0.54 g-atom) of lithium and 0.037 g of sodium by vigorous stirring under anhydrous dodecane at reflux temperature for 10 min in a 500-mL Morton flask equipped with a high-speed stirrer.[34] Stirring was stopped and the mixture cooled to room temperature before the dodecane was removed with a cannula and the lithium sand was rinsed with 200 mL of freshly distilled ether. A final 200 mL of ether was added, stirring was recommenced, and 0.2 mL of methyl iodide and 2 mL of a solution of 5.45 g (0.0212 mol) of the *trans* chloride **7** in 40 mL of ether was added at room temperature to initiate reaction. After 5 min of reaction, the solution began to develop a light green coloration and the temperature was lowered to -75 °C by means of a dry ice–acetone bath. The remainder of the solution of **7** was added dropwise over a period of 20 min, and stirring was continued for 2.5 h more at -75 °C before the reddish-brown contents of the flask were forced onto solid carbon dioxide. The residual contents of the flask were stirred with 200 mL of additional anhydrous ether at -75 °C and also forced onto the solid carbon dioxide. The carbonated mixture was treated with enough 5% aqueous HCl to make the pH 1, saturated with NaCl, and extracted three times with ether. The ethereal solution of product was then separated into neutral and acidic products by standard acid–base extraction procedures. The acidic product according to quantitative GC analysis contained 0.14 g (2.5%) of **32**, 0.10 g (1.8%) of **11a**, 2.1 g (37%) of **14a**, and 0.07 g (1.2%) of **17**. Recrystallization of the crude acid from acetone gave 1.4 g of white crystals, identical in physical properties with those of the authentic sample of **14a**.

Run 2 was conducted with 1.7 g of lithium sand (0.24 g-atom, 1% Na) and 2.09 g (8.14 mmol) of **7** at -75 °C exactly as in run 1. When the reaction of the chloride was completed, the solution was warmed to 0 °C and held at this temperature for 1.5 h by means of an ice bath prior to carbonation. Quantitative GC analysis gave 0.03 g (1.4%) of **32**, 0.45 g (21%) of **11a**, 0.54 g (25%) of **14a**, and 0.02 g (0.9%) of **17**.

Run 3 with 4.0 g of Li (1% Na) and 4.95 g (19.3 mmol) of **7** was conducted at -75 °C just as in run 1, whereupon half of the solution was carbonated (aliquot A), and the remainder was then held at 35 °C (reflux) for 3 h before carbonation of the dark orange solution (aliquot B). According to quantitative GC analysis, aliquot A contained 0.11 g (2.1%) of **32**, 0.14 g (2.7%) of **11a**, 0.24 g (4.7%) of **14a**, and 0.014 g (0.27%) of **17**; aliquot B contained 2.09 g (41%) of **11a**, 0.16 g (3%) of **17**, and 0.07 g (1.3%) of **18**. The low yields from aliquot A are taken to imply that the organolithium reagent is not very soluble in diethyl ether (275 mL) at -75 °C. Recrystallization of 2.0 g of the crude product from aliquot B from aqueous ethanol gave 1.5 g of pure crystalline **11a**, identical in spectral properties with the synthetic sample.

Run 4 with 2.5 g of Li (1.4% Na) and 2.51 g (9.78 mmol) of **7** was conducted in 350 mL of ether as in run 3 with carbonation of 40% of the solution after 4 h at -75 °C (aliquot A) and the remainder of the solution after 4 h at 35 °C (aliquot B). Aliquot A yielded 0.50 g of crude acid, which by GC and ^1H NMR analyses contained 3% of **13a**, 10% of **11a**, 49% of **14a**, 1% of **17**, and 34% of **32**. Aliquot B yielded 0.95 g of acids whose composition is given in Table I.

Run 5, with 5.0 g of lithium (1% Na) and 4.02 g (15.6 mmol) of **7** in 200 mL of THF, was initiated at 0 °C by addition of 0.1 mL of CH_3I and four drops of the solution of **7** in 50 mL of THF. Upon appearance of a pinkish-orange color, the temperature was lowered to -75 °C, and the remainder of the chloride was added dropwise over a period of 30 min. After 1 h a small ^1H NMR aliquot (protonated) indicated that reaction of the chloride was complete. After 30 more minutes, approximately 100 mL of the solution was carbonated (aliquot A), 125 mL was stirred for 8 more hours at -75 °C before carbonation (aliquot B), and the remaining 125 mL of solution was warmed to 1.0 ± 3 °C and kept at this temperature for 4 h before carbonation (aliquot C). The usual workup of the carbonated aliquots gave 0.80 g (A), 1.82 g (B), and 0.94 g (C) of crude acids whose compositions are given in Table I. Unknown A has GC–MS (electron impact) *m/e* (relative intensity) 233 (15), 218 (7), 215 (13), 207 (12), 206 (10), 207 (7), 205 (11), 197 (12), 191 (9), 189 (22), 178 (16), 175 (20), 165 (15), 162 (100), 148 (16), 147 (75) and, by chemical ionization using isobutene, 181 (100, M + 1); this spectrum, especially the base peak at 162, suggests the structure $CH_3O_2CCPh(CH_3)CHPhCH{=}CH_2$.

In run 6, 5.6 g of lithium (1% Na) was allowed to react with 4.02 g (15.7 mmol) of **7** in 290 mL of THF at −75 °C according to the procedures of run 5. After 3 h of reaction, about one-third of the solution was carbonated (aliquot A). To the remainder of the reaction solution was added 34.4 mmol of potassium *tert*-butoxide (freshly prepared) in 140 mL of THF (cooled to −75 °C), and the solution was stirred for 1 h at −75 °C before carbonation. The product compositions are given in Table I.

Run 7 with 1.70 g of lithium (1% Na) and 2.55 g (9.93 mmol) of cis chloride **2** was conducted in 350 mL of diethyl ether at −75 °C as in run 1. After 4 h at −75 °C, about a 100-mL aliquot (A) was carbonated and then the remainder was held at 35 °C for 4 h before carbonation (aliquot B). Aliquots A and B yielded 0.65 and 1.11 g of crude acids, respectively, whose compositions are listed in Table I.

Run 8 with 1.68 g of lithium (0.242 g-atom) and 2.51 g (9.76 mmol) of cis chloride **2** in 350 mL of THF was initiated as in run 5 and then allowed to react for 3 h at −75 °C before carbonation of a 140-mL aliquot A. The remainder of the solution was held at 0 ± 5 °C for 4 h before carbonation (aliquot B). Aliquots A and B yielded 0.65 and 1.20 g of crude acids, respectively (see Table I). Unknown B in aliquot B came as a separate GC peak right after the methyl ester of *trans*-5,5-diphenyl-3-hexenoic acid (**43**) and has MS of *m/e* (relative intensity) 206 (100), 205 (20), 191 (34), 165 (8), 143 (14), 129 (45), 128 (20), 115 (11), 105 (13), 91 (54); this MS is essentially identical to that of **43** (given below), and therefore unknown B is likely *cis*-5,5-diphenyl-3-hexenoic acid (**45**). Crude acid from aliquot B was dissolved in hot *n*-pentane. Crystals (mp 126–137 °C) were deposited at room temperature; these, by ^{1}H NMR analysis, consisted of a 45:55 ratio of **43**:**10a**. The pentane solution after 12 h at 0 °C deposited additional crystals (mp 101–103 °C), which by ^{1}H NMR analysis consisted of a 95:5 ratio of **43**:**10a**. The major component **43** has ^{1}H NMR (60 MHz, CCl_4) at δ 1.78 (s, 3 H, CH_3CPh_2), 3.13 (d of d, J = 1.2 and 6 Hz, 2 H, $CH{=}CHCH_2CO_2H$), 5.33 (d of t, J = 6 and 15 Hz, 1 H, $CH{=}CHCH_2$), 6.13 (d of t, J = 1.2 and 15 Hz, 1 H, $CH{=}CHCH_2$), 7.12 (br s, 10 H, Ar*H*). For methyl ester of **43**: MS M$^+$ calcd for $C_{19}H_{20}O_2$, 280.1463; found 280.1463; *m/e* (relative intensity) 280 (1.3), 206 (100), 205 (16), 191 (39), 165 (10), 143 (13), 129 (50), 128 (23), 115 (14), 105 (9), 91 (50).

Rearrangement of [(*E*)-2,2-Diphenyl-3-pentenyl]lithium (15) in the Presence of *n*-Butyllithium. The organolithium compound (**15**) was prepared from 7.04 g (27.4 mmol) of **7** and 5.9 g (0.85 mol) of lithium sand (1% Na) in 500 mL of diethyl ether at −75 °C according to the usual procedure; however, since reaction ceased after 4 h at −75 °C (25% reaction), the temperature was raised to −50 °C, and freshly cut pieces of lithium wire (6.2 g) were added. After 10 hours of reaction at −40 to −50 °C, reaction was complete, and a 75 mL aliquot A was carbonated. Another 75-mL aliquot (B) was held at −22 °C for 27 h before carbonation. A final 125-mL aliquot (C) was cooled to −75 °C, 8.0 mL (13.3 mmol) of *n*-butyllithium in hexane (−75 °C) was added, and the solution then held at 35 °C (reflux) for 5 hours before carbonation. Aliquot A yielded 0.44 g of acids: 58% (**14a**), 37% (**11a**), 1% (**18**), and 3% (**17**); aliquot B 0.36 g of acids: 33% (**14a**), 62% (**11a**), 1% (**19**), and 3% (**17**); aliquot C 1.1 g of acids: 91% (**11a**), 3% (**18**), and 5% (**17**). Aliquot C after removal of valeric acid (in vacuo) gave no ^{1}H NMR evidence for 2,2-diphenylheptanoic acid in the region δ 0.8–1.4 expected for a terminal *n*-butyl group. Also analysis of the methyl esters of the product from aliquot C by GC–MS failed to show an ester of *m/e* corresponding to methyl 2,2-diphenylheptanoate either by electron impact or chemical ionization techniques. Hence the amount of *n*-butyl incorporation in the product acids, if any, must have been less than one or two percent.

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Supplementary Material Available: Detailed procedures for preparation of **21b**, **22b**, **24b**, **25b**, **28**, **29b**, **31**, and **32**; a description of the crystal structure determination for **24b** including tables of atomic coordinates, bond distances, and angles; and a perspective view of the structure drawn with the ORTEP program (14 pages). Ordering information is given on any current masthead page.