is representative. Into a three-necked 500-mL, round-bottomed flask, equipped with a cold-finger condenser charged with solid CO_2 and ethanol, a nitrogen inlet, and a magnetic stirrer, was condensed ~250 mL of ammonia. To the ammonia was added *t*-BuOH (9.74 mmol) and Na metal (9.74 mol) to form sodium *tert*-butoxide and then $PhCH_2SH$ (9.74 mmol). To this solution was added 2-chloroquinoline (4.86 mmol), and the solution was irradiated for 90 min. The reaction was quenched by adding MeI (9.7 mmol), and the ammonia was allowed to evaporate. Water (100 mL) was added to the residue, and the mixture was extracted three times with 50 mL of diethyl ether. The ether extracts were dried and distilled. The residue was column-chromatographied on silica gel and eluted with petroleum ether. 2-Quinolyl benzyl sulfide was obtained as a white solid and was recrystallized from petroleum ether: mp 39–41 °C (lit.[25] mp 44–45 °C); hydrochloride, mp 183–186 °C (lit.[25] mp 187–190 °C); NMR δ 4.48 (s, 2 H), 6.6–6.8 (m, 11 H); mass spectrum, *m/e* (relative intensity) 251 (100), 218 (75), 160 (12), 129 (50), 116 (12), 91 (75).

The photostimulated reaction with methanethiolate ion was quenched with benzyl chloride and quantified by GC (1-chloronaphthalene as internal standard). The photostimulated reaction of 2-chloropyridine with *n*-butanethiolate ion was quenched with benzyl chloride, and the products were column chromatographed on silica gel and eluted with petroleum ether. *n*-Butyl 2-pyridyl sulfide [NMR δ 0.5–1.8 (m, 7 H), 2.8–3.3 (m, 2 H), 6.5–8.4 (m, 4 H)] and 2-pyridyl benzyl sulfide [NMR δ 3.46 (s, 2 H), 6.6–7.3 (m, 9 H)] were isolated.

The photostimulated reaction of *t*-BuS^- ion with iodobenzene was quenched with benzyl chloride, and the products were quantified by GC, with 1-chloronaphthalene as internal standard, and compared with authentic samples. The photostimulated reaction of 1-iodonaphthalene and *t*-BuS^- ion gave only the substitution product, *tert*-butyl 1-naphthyl sulfide, which was isolated by column chromatography (silica gel, eluted with petroleum ether) as a white solid and recrystallized from petroleum ether: mp 55–56 °C; NMR δ 1.26 (s, 9 H), 7.2–8.7 (m, 7 H); mass spectrum, *m/e* (relative intensity) 216 (65), 161 (36), 160 (100), 128 (24), 115 (100).

The photostimulated reaction of iodobenzene and $PhCH_2S^-$ ion was quenched with MeI, and by GC (internal standard 1-methylnaphthalene) there was obtained only methyl phenyl sulfide (4% yield). The photostimulated reaction of 2-chloropyridine with the same nucleophile was quenched with MeI. The products were column chromatographed (silica gel, eluted with petroleum ether) and gave 2-pyridyl benzyl sulfide and 2-pyridyl methyl sulfide: NMR δ 2.53 (s, 3 H), 6.6–8.4 (m, 4 H). The photostimulated reaction with 1-bromonaphthalene (quenched with MeI) was analyzed by GC/MS: 1-naphthyl benzyl sulfide, *m/e* (relative intensity) 250 (8), 115 (16), 91 (100), 65 (15); 1-naphthyl methyl sulfide, *m/e* (relative intensity) 174 (82), 159 (50), 115 (100); dibenzyl sulfide, *m/e* (relative intensity) 214 (79), 91 (100), 65 (24). The dark reaction of $PhCH_2S^-$ ion with 2-chloroquinoline was quenched with MeI and analyzed by GC with 2-methylnaphthalene as an internal standard. The photostimulated reaction with 9-bromophenanthrene was analyzed by GC.

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Registry No. PhI, 591-50-4; 2-ClPyr, 109-09-1; 1-INaph, 90-14-2; 1-ClNaph, 90-13-1; 1-BrNaph, 90-11-9; 9-BrPhen, 573-17-1; 2-ClQ, 612-62-4; PhS^-, 13133-62-5; MeS^-, 17302-63-5; EtS^-, 20733-13-5; *n*-BuS^-, 20733-16-8; *t*-BuS^-, 20733-19-1; $PhCH_2S^-$, 1492-49-5; $HOCH_2CH_2S^-$, 57966-62-8; phenyl radical, 2396-01-2; 2-pyridyl radical, 15905-71-2; 1-naphthyl radical, 2510-51-2; 9-phenanthryl radical, 20199-82-0; 2-quinolyl radical, 54978-39-1.

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Alkylation of Allylic Derivatives. 3. The Regiochemistry of Alkylation of the Isomeric *trans*-α,γ-Methylphenylallyl Acetates with Lithium Dialkylcuprates

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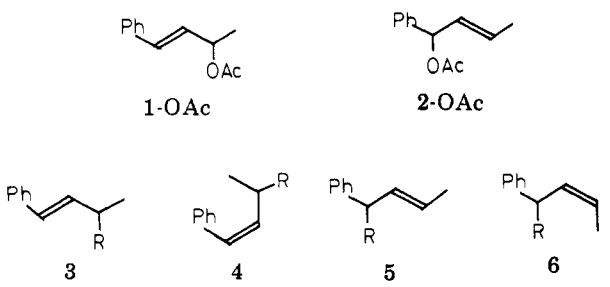
Alkylation of the isomeric *trans*-α,γ-methylphenylallyl acetates (**1**-OAc and **2**-OAc) with lithium dimethylcuprate or di-*n*-butylcuprate is regioselective but not regiospecific. Both isomers give essentially the same product mixture which contains 95% of the trans conjugated alkylation product (**3**). The starting acetates do not rearrange under the conditions for these reactions. These results show that the isomeric acetate give the same product-forming intermediate(s). Presumably the key intermediate that is common to the two isomers is a π-allyl copper(III) complex (**7**).

We have extended our studies[1] of the regio- and stereochemistry of alkylation of allylic derivatives with organocopper reagents to the *trans*-α,γ-methylphenylallyl system. This paper reports an investigation of the regiochemistry of alkylation of the isomeric acetates (**1**-OAc and **2**-OAc) with lithium dimethylcuprate and di-*n*-butylcuprate. Possible alkylation products include two conjugated isomers, (*E*)- and (*Z*)-3-alkyl-1-phenyl-1-butene (**3** and **4**) and two unconjugated isomers, (*E*)- and (*Z*)-1-alkyl-1-phenyl-2-butene (**5** and **6**).

Product distributions for alkylation of the acetates in ether at 0 °C are presented in Table I. These compositions were determined by capillary GC and in all cases base line resolution of all components was observed. The yields included in the table are GC yields obtained with (*E*)-1-phenyl-1-pentene as an internal standard for the **3a–5a** mixtures and 1-phenyloctane for the **3b-5b** mixture. Mixtures were isolated in yields of 64–68%. Normally only **3**, **4**, and **5** were detected in product mixtures and unidentified contaminants, if any, were present in only trace amounts. (*Z*)-1-Alkyl-1-phenyl-2-butene (**6**) was not de-

(1) Previous paper in this series is Goering, H. L.; Kantner, S. S. *J. Org. Chem.* **1981**, *46*, 2144.

0022-3263/81/1946-5304$01.25/0



a, R = Me; R = *n*-Bu

tected in any of the experiments.

Lithium dimethylcuprate was prepared by adding slightly less[2] than 1 equiv of methyllithium to a suspension of methylcopper in ether, which in turn was prepared either from a butyl sulfide–copper iodide complex[3] or a cuprous iodide slurry. The source of the methylcopper had no effect on product distributions. Lithium di-*n*-butylcuprate was prepared by addition of slightly less than 2 equiv of butyllithium to cuprous iodide. Thus for each cuprate, just under 2 equiv of alkyllithium was used for each equivalent of copper. Evidently, the cuprates are largely or completely dimeric under the conditions of the alkylation reactions.[4]

As shown by the yields in Table I, reaction of the acetates with 2 equiv of $LiCuMe_2$ in ether at 0 °C for 10 min results in essentially quantitative conversion to the **3a–5a** mixture. With 1 equiv of cuprate, yields decrease to 70–80% and are not improved by increasing the reaction time. Yields are somewhat lower for alkylation with $LiCu(n\text{-}Bu)_2$. In this case there is a small improvement (from 82% to 86%) by a 12-fold increase in reaction time. However, increasing the cuprate/acetate ratio from 2 to 4 has no effect on yield. Variation of the cuprate/substrate ratio had no significant effect on product distributions.

Alkylation products were identified by comparison with authentic samples. The major product, **3**, was readily isolated in pure form from reaction mixtures by preparative GC. Authentic samples of **3a** and **3b** were obtained as follows. A mixture of (*Z*)- and (*E*)-3-methyl-1-phenyl-1-butene (**3a** and **4a**) was obtained by a Wittig reaction as reported earlier,[5] and homogeneous samples of **3a** and **4a** were isolated from this mixture by preparative GC. These isomers were readily identified by their NMR and IR spectra. Pure samples of (*Z*)- and (*E*)-3-methyl-1-phenyl-1-heptene (**3b** and **4b**) were prepared and identified in a similar manner.

The minor components in the alkylation products (**4a** and **4b**) could not be isolated from the mixtures in pure form and were identified by comparison of capillary GC retention times with those of authentic samples. Similarly, **5** could not be isolated from the product in pure form.

(*E*)-4-Phenyl-2-pentene (**5a**) was identified as follows. An 84:16 binary mixture of **5a** and **4a** was isolated from the $LiCuMe_2$ alkylation product by preparative GC. The NMR spectrum of the major component of this mixture was determined from that of the mixture and that of the minor component (**4a**) and corresponded to structure **5a**, e.g., the coupling constant of the vinyl protons is 15.2 Hz. Also, the strong IR absorption at 960 cm^{-1} indicates the *E* configuration—**4a** has no IR absorption in this region.

Table I. Product Distributions for Alkylation of Isomeric *trans*-α,γ-Methylphenylallyl Acetates (1-OAc and 2-OAc) with $LiCuMe_2$ and $LiCu(n\text{-}Bu)_2$ in Ether at 0 °C[a]

acetate	cuprate[b]	product distribution, % 3	4	5	6	% yield[c]
1-OAc[d]	$LiCuMe_2$	95	<1	4.1	0	99–100
2-OAc[d]	$LiCuMe_2$	95	<1	4.4	0	96–100
1-OAc[e]	$LiCuBu_2$	93.6	0.6	5.8	0	82–86
2-OAc	$LiCuBu_2$	92.8	0.6	6.6	0	81

[a] Reaction time was 10 min in each experiment. [b] Cuprate/acetate ratio was 2 for all cases. [c] GC yields. (*E*)-1-Phenyl-1-pentene internal standard for alkylation with $LiCuMe_2$ and 1-phenyloctane internal standard for alkylation with $LiCu(n\text{-}Bu)_2$. [d] Average of four independent experiments. Deviations less than 0.1% for all components. [e] Average of three independent experiments.

Hydrogenation of the binary mixture gave an 84:16 mixture of 2-phenylpentane and 1-phenyl-3-methylbutane.

The structure of **5a** was confirmed by independent synthesis as follows. The Wittig reaction[6] of ethylidenetriphenylphosphorane and 2-phenylpropionaldehyde gave a 12:88 mixture of *E* (**5a**) and *Z* (**6a**) isomers. A second procedure,[7] which normally favors the *E* isomer, gave a 20:80 mixture of **5a** and **6a** (the latter mixture had a more intense IR band at 960 cm^{-1}). Homogeneous samples of **5a** and **6a** could not be separated from the binary mixture of authentic samples. However, the NMR spectrum of **6a** could be deduced from that of the mixture and the spectrum of the minor component, **5a**. Hydrogenation of the synthetic mixture of **5a** and **6a** gave 2-phenylpentane.

(*E*)-4-Phenyl-2-octene (**5b**) in the $LiCu(n\text{-}Bu)_2$ alkylation product was identified as follows. In work to be reported elsewhere[8] it has been found that alkylation of 1-OAc with lithium *n*-butylcyanocuprate is regiospecific and gives mixtures containing >50% **5b**. Similarly, alkylation of 1-OH with butyllithium by the Murahashi[9] method gives mixtures containing large amounts of **5b**.[1] A 76:24 binary mixture of **5b** and **6b** was isolated from such mixtures by preparative GC. Attempts to separate these isomers by GC were unsuccessful; however, base line resolution was achieved with capillary GC. A 270-MHz NMR spectrum with vinyl methyl protons decoupled showed the major and minor components to be **5b** (vinyl protons coupling 15.2 Hz) and **6b** (vinyl protons coupling 10.7 Hz). Diimide reduction of the mixture gave a single compound, 4-phenyloctane, which was identified by comparison with an authentic sample prepared by alkylation of 1-phenyl-*n*-butyl bromide with $LiCu(n\text{-}Bu)_2$.

Structural assignments for **5b** and **6b** were confirmed by synthesis of an authentic mixture of the isomers. The Wittig reaction[6] of ethylidenetriphenylphosphorane and 2-phenylhexanal gave a 32:68 mixture of **5b** and **6b**. The major and minor components of this mixture were identified as **5b** and **6b** by the decoupled 270-MHz NMR spectrum.[10] The NMR properties and GC retention time for **5b** in this mixture were the same as for the component in the alkylation mixture assigned this structure. This mixture was converted to 4-phenyloctane by reduction with diimide.

(2) Carbonyl attack with formation of the corresponding alcohol accompanies alkylation if the MeLi/MeCu ratio is >1.
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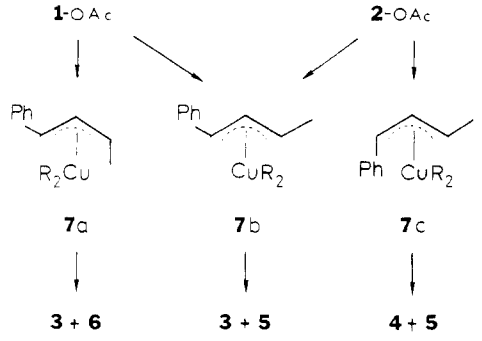
(8) Tseng, C. C., unpublished work in these laboratories.
(9) Tanigawa, Y.; Ohta, H.; Sonoda, A.; Murahashi, S.-I. *J. Am. Chem. Soc.* **1978**, *100*, 4610.
(10) A distinguishing feature of NMR spectra of **5b** and **6b** that can be readily seen in 100-MHz spectra of mixtures is that the methine proton signal (br q) for the *E* isomer (**5b**) is centered at 3.14 ppm and that for the *Z* isomer (**6b**) is centered at 3.55 ppm.

Scheme I. Isomeric π-Allyl Complexes and Possible α- and γ-Alkylation Products Derived from 1-OAc and 2-OAc



The results in Table I show that the alkylation reactions are regioselective (preferential formation of the *E* conjugated isomer, **3**) but not regiospecific (both acetates give the same product distribution). At −78 °C the two acetates also give the same product mixture and the composition is similar to that for alkylation at 0 °C.

That the same product mixture for the two acetates does not result from allylic rearrangement prior to alkylation was established as follows. The unconjugated acetate (**2**-OAc) was reacted with less than the amount of $LiCuMe_2$ required for complete alkylation and the unreacted acetate was isolated and examined by NMR analysis.[11] In the presence of a shift reagent, $Eu(fod)_3$, the acetyl methyl singlets for the isomers are completely separated and spectra of synthetic mixtures showed that 3% intercontamination can be detected by this method. Europium shift reagents catalyze the **2**-OAc → **1**-OAc isomerization in NMR solvents.[12] However, this isomerization is slow and with proper choice of concentrations there is ample time for NMR analysis of the acetates. In these experiments the isolated unreacted **2**-OAc was found to be unchanged.

Incomplete alkylation also results if the alkylating reagent is prepared with a MeLi/MeCu ratio of 0.5 instead of 1. In this case the reagent is presumably $LiCu_2Me_3$.[4] Under these conditions both acetates also give the same product distribution. In all cases the unreacted acetate was unchanged.

In related studies the alcohol resulting from carbonyl attack associated with alkylation[2] was examined by silylation followed by analysis of the silyl derivative by GC.[11] The introduction of carbonyl attack[2] had no effect on the composition of the alkylation product, and in all cases, the alcohol had the same allylic structure as the starting acetate.

These experiments show that loss of regiochemistry does not result from loss of allylic structure prior to alkylation. Instead, allylic structure is lost during alkylation. Put another way, the isomeric acetates give the same intermediate(s). We believe the common intermediate is a π-allylcopper(III) complex (**7**) which results from oxidative addition of the acetate to the cuprate (probably via copper(I)–olefin π complexes).[1]

Evidently the original double bond configuration is preserved in the π-allyl complex.[1] Thus each acetate can give two isomeric complexes as illustrated in Scheme I. The reactive conformations[1] for **1**-OAc are related to **7a** and **7b** and the reactive conformations for **2**-OAc are related to **7b** and **7c**. The alkylation products derived from the isomeric complexes are shown in the scheme.

Product distributions in Table I indicate that almost all of the product is derived from **7b** and a minor amount from **7c**. The presence of **4** in product derived from **2**-OAc is not unexpected because in this case this is a γ-alkylation product and γ-alkylation generally gives a mixture of *E* and *Z* isomers.[1] However **4**, which is definitely present in minor amounts, is not an expected product for **1**-OAc because in other cases (including the *cis*-cinnamyl system)[13] α-alkylation apparently proceeds with complete preservation of double bond configuration.[1]

It should be noted that the presence of **4** in product obtained from **1**-OAc does not necessarily result from α-alkylation with partial loss of double bond configuration. This could well be an artifact that results from contamination of the starting acetate (**1**-OAc) with trace amounts of the cis isomer. Attempts to develop a method for detecting such contamination were unsuccessful.[11]

Experimental Section

Materials. Ethyl ether was distilled from lithium aluminum hydride. Cuprous iodide was purified by a published method.[14] Solutions of *n*-butyllithium in hexane[15] and methyllithium in ether[16] were frequently standardized.

(*E*)-1-Phenyl-1-pentene (internal standard for analysis of **3a–5a** mixtures) was obtained from an *E–Z* mixture (50% *Z* isomer) prepared by the Wittig reaction of benzyltriphenylphosphonium chloride and butyraldehyde.[5,17] Homogeneous samples of the isomers were separated by preparative GC (5 ft × $^3/_8$ in. column, 24% SF-96 on Chromosorb P, 130 °C). That the isomers were homogeneous was established by capillary GC (94-ft column, UCON LB 550X, 120 °C). Spectral data for (*E*)-1-phenyl-1-butene were the same as published data.[18]

(*Z*)-1-Phenyl-1-pentene[5] isolated from the Wittig mixture had the following: IR (neat) 3070, 3050, 3000, 2950, 2920, 2870, 1640, 1600, 1570, 1490, 1460, 1450, 1445, 1405, 1375, 1330, 1315, 1265, 1150, 1070, 1025, 910, 865, 790, 760, 690 cm^{-1}; NMR ($CDCl_3$) δ 7.4–7.5 (m, 5 H), 6.40 (dt, 1 H, *J* = 11.5, 1.5 Hz), 5.64 (dt, 1 H, *J* = 11.5, 7 Hz), 2.4–2.12 (br q, 2 H), 1.68–1.24 (br sextet, 2 H), 0.92 (t, 3 H, *J* = 7 Hz).

α-Methyl-γ-phenylallyl alcohol (1-OH), bp 99–100 °C (1.4 mm), mp 34–36 °C [lit.[19] bp 93–94 °C (1.5 mm); mp 33.5–34.5 °C] was prepared from cinnamaldehyde and methylmagnesium iodide as reported earlier.[19,20] Spectral data were the same as for samples prepared for an earlier study.[20]

α-Phenyl-γ-methylallyl alcohol (2-OH), bp 82 °C (1.7 mm), was prepared from crotonaldehyde and phenylmagnesium bromide as reported earlier.[20,21] For some of the experiments, **2**-OH was purified via the *p*-nitrobenzoate derivative. The latter was hydrolyzed by the procedure used earlier for saponification of the acid phthalate derivative.[12,22] Spectral data for **2**-OH were the same as for samples prepared for another investigation.[20,22]

α-Methyl-γ-phenylallyl acetate (1-OAc) was prepared from pure **1**-OH and acetic anhydride in dry pyridine. After vacuum distillation **1**-OAc was obtained as a colorless oil: bp 102 °C (2

(11) Gas chromatography was not applicable for analysis of the allylic acetates (**1**-OAc and **2**-OAc) or the corresponding alcohols. The acetates and alcohols give a single peak with the same retention time. Evidently all decompose to the same product in the injection port.

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(21) Exposure of **2**-OH and **2**-OAc to acid was carefully avoided and the apparatus used for preparation and handling of these compounds was soaked in ammonia water prior to drying.

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mm) [lit.[23] bp 132–133 °C (9 mm)]; IR ($CHCl_3$) 3080, 3050, 3010, 2980, 2930, 2870, 1720, 1650, 1595, 1570, 1490, 1440, 1370, 1270–1210, 1145, 1035, 960, 945 cm^{-1}; UV (ethanol) λ_{max} 250 nm (log ϵ 4.2); NMR ($CDCl_3$) δ 7.6–7.2 (m, 5 H), 6.67 (d, 1 H, J = 15 Hz), 6.23 (dd, 1 H, J = 7, 15 Hz), 5.57 (quintet, 1 H, J = 7 Hz), 2.05 (s, 3 H), 1.40 (d, 3 H, J = 7 Hz).

α-Phenyl-γ-methylallyl acetate (2-OAc) was prepared from pure **2-OH** by the procedure used to prepare **1-OAc**.[21] After distillation at reduced pressure, **2-OAc** was obtained as a colorless oil: bp 86–88 °C (1.8 mm) [lit.[23] bp 123 °C (11 mm)]; IR ($CHCl_3$) 3080, 3060, 3010, 2960, 2940, 2910, 2875, 2850, 1720, 1665, 1490, 1445, 1430, 1365, 1250–1200, 1100, 1060, 1010, 955 cm^{-1}; UV (ethanol) λ_{max} 252 nm (log ϵ 3.0); NMR ($CDCl_3$) δ 7.6–7.0 (m, 5 H), 6.44–6.28 (m, 1 H), 5.95–5.55 (m, 2 H), 2.05 (s, 3 H), 1.85–1.65 (m, 3 H). These spectral data are the same as for a sample of **2-OAc** prepared for an earlier study.[12]

(*E*)-1-Phenyl-1-[(trimethylsilyl)oxy]-2-butene (2-OTMS) was prepared from **2-OH** by a standard procedure.[24] This silyl derivative had the following: bp 59 °C (0.7 mm); IR (neat) 3080, 3060, 3020, 2955, 2915, 2855, 1665, 1600, 1490, 1450, 1375, 1300, 1250, 1195, 1125, 1090, 1070, 1050, 1025, 1005, 960, 905, 880, 835, 745, 695 cm^{-1}; NMR (CCl_4, CH_2Cl_2 reference) δ 7.58–7.13 (m, 5 H), 5.85–5.63 (m, 2 H), 5.30–5.13 (m, 1 H), 1.96–1.76 (m, 3 H), 0.27 (s, 9 H). Anal. Calcd for $C_{13}H_{20}OSi$: C, 70.85; H, 9.15; Si, 12.74. Found: C, 70.99; H, 9.03; Si, 12.63.

(*E*)-1-Phenyl-3-[(trimethylsilyl)oxy]-1-butene (1-OTMS) was prepared in the same way: bp 78 °C (1.1 mm); IR (neat) 3075, 3055, 3020, 2960, 2920, 2895, 2860, 1600, 1575, 1495, 1450, 1365, 1360, 1330, 1310, 1295, 1250, 1200, 1145, 1080, 1025, 995, 960, 920, 900, 835, 745, 685 cm^{-1}; NMR (CCl_4, CH_2Cl_2 reference) δ 7.40–7.0 (m, 5 H), 6.58 (d, 1 H, J = 16 Hz), 6.26 (dd, 1 H, J = 6, 16 Hz), 4.56 (quintet, 1 H, J = 6 Hz), 1.43 (d, 3 H, J = 6 Hz), 0.30 (s, 9 H). Anal. Calcd for $C_{13}H_{20}OSi$: C, 70.85; H, 9.15; Si, 12.74. Found: C, 70.97; H, 8.95; Si, 12.52.

Alkylation of *trans*-Methylphenylallyl Acetates 1-OAc and 2-OAc. A. Alkylation with $LiCuMe_2$. All reactions were carried out under dry nitrogen. The following is a typical experiment. A test tube containing a small magnetic stirring bar was charged with 0.191 g (1.003 mequiv) of Cu_2I_2 (or an equivalent amount of butyl sulfide–copper iodide complex)[3] and fitted with a rubber septum. The tube was flushed with dry nitrogen and charged with 5 mL of dry ether. The mixture was cooled in a dry ice–acetone bath and 0.56 mL of 1.7 M ethereal MeLi (0.95 mmol) was added. The mixture was stirred at −78 °C for ~20 min and centrifuged, and the supernatant liquid was removed with a cannula. The yellow precipitate was washed with three 5-mL portions of dry ether as follows. The ether was added, the resulting mixture was stirred a few minutes at −78 °C, and after the mixture was centrifuged the supernatant liquid was removed. After addition of 5 mL of dry ether to the yellow MeCu precipitate, a second 0.56-mL portion of ethereal MeLi (0.95 mmol) was added and the stirred mixture was allowed to warm to 0 °C. To the resulting clear solution of $LiCuMe_2$ was added 0.089 g (0.47 mmol) of **1-OAc** or **2-OAc** in 0.5 mL of ether. The loaded syringe containing the ethereal solution of the acetate was precooled to 0 °C in a chilled desiccator. The reaction mixture was stirred for 10 min at 0 °C and then quenched by addition of 0.5 mL of water. An ethereal solution of the internal standard, (*E*)-1-phenyl-1-pentene, was added and the resulting mixture was centrifuged. The organic layer was removed from the solids with a pipet, dried (K_2CO_3), and concentrated by rotary evaporation at room temperature for 2–3 min. Yields and product distributions were determined by capillary GC (94-ft column, UCON LB 550X, 90 °C). Typically, each sample was analyzed 3 times and average peak areas (from electronic integration) were used to compute yields and product distributions. Under these conditions the internal standard has a longer retention time than any of the alkylation products. Results of these experiments are presented in Table I.

When half of the above amount of cuprate was used (i.e., 0.5 mmol of cuprate for alkylation of 0.5 mmol of **1-OAc**), unreacted acetate was present in the reaction mixture. The composition of the acetate was determined as follows. After concentration of the product mixture by rotary evaporation at room temperature, the residue was concentrated under vacuum (0.6 mm) for an additional 10 min. This left 0.206 g of residual oil. The NMR spectrum indicated this material to be essentially a 1.6:1 molar ratio of unreacted acetate to **3a**. Control experiments showed that addition of 0.05 g of $Eu(fod)_3$ to 0.05 g of **2-OAc** in 0.5 mL of $CDCl_3$ gives suitable shifted NMR spectra and that the **2-OAc** → **1-OAc** isomerization is slow (<5% in 10 min). These experiments also showed that the acetyl methyl singlets are completely separated for the isomers (that for **1-OAc** is downfield) and that there is no interference from any of the alkylation products **3a–5a**. An NMR tube was charged with 0.04 g of $Eu(fod)_3$ and 0.07 g of the concentrated reaction mixture in 0.5 mL of $CDCl_3$. The spectrum in the region of the shifted acetyl methyl signals was scanned repeatedly for a period of ~45 min. The first scans showed no evidence for the presence of **1-OAc**. The signal for **1-OAc** appeared after ~15 min (<3% of acetate was **1-OAc**) and after 45 min the **1-OAc**/**2-OAc** ratio was ~1:22.

Unreacted acetate was also observed when the MeLi/MeCu ratio was 0.5 instead of 1. In these experiments NMR spectra shifted with $Eu(fod)_3$ also showed the unreacted acetate (**1-OAc** or **2-OAc**) to be unchanged.

Carbonyl attack with formation of alcohol resulted when the MeLi/MeCu ratio was 2 instead of 1. In these experiments reaction mixtures were worked up as usual. A slight excess of silylating reagent[24] was added to the residual reaction mixture. After the mixture was stirred for 3 h at room temperature, the reaction was quenched with water and the mixture extracted with 2 mL of pentane. The pentane solution was washed with water, cold dilute HCl, and finally with saturated aqueous $NaHCO_3$. After the solution dried, the composition of the silyl derivative was determined by GC (5-ft column, 3% SE-30 on Varaport No. 30, 100–200 mesh, 90 °C). In all cases the silyl derivative of alcohol produced by carbonyl attack had the same allylic structure as the starting acetate.

Control experiments showed that under these conditions silyl derivatives have the same compositions as mixtures of **1-OH** and **2-OH** from which they are prepared. Also, this is a reliable method for detecting small amounts (1–3%) of intercontamination of the isomeric alcohols.[11]

B. Alkylation with $LiCu(n\text{-}Bu)_2$. In a typical experiment a 25-mL flask equipped with magnetic stirrer and septum was charged with 0.191 g of Cu_2I_2 (1.003 mequiv). After the apparatus was flushed with dry nitrogen, 5 mL of dry ether was added and the flask was chilled to −78 °C. To the chilled mixture was added 1.2 mL of *n*-butyllithium in hexane (1.9 mmol) and the resulting gray mixture was stirred 30 min at −78 °C and then warmed to 0 °C. The resulting dark-purple solution was stirred an additional 10 min after which a precooled (0 °C) solution of 0.089 g (0.47 mmol) of acetate (**1-OAc** or **2-OAc**) in 0.5 mL of anhydrous ether was added. After the mixture was stirred for 10 min, the reaction was quenched with 0.5 mL of water and then 10 mL of pentane containing the internal standard, 1-phenyloctane (Aldrich), was added. The reaction mixture was worked up as described in part A except that solids formed during quenching were removed by filtration instead of centrifugation. Compositions of the **3b–5b** mixtures were determined by capillary GC (94-ft column, UCON LB 550X, 130 °C). This column does not separate **5b** and **6b**; however, base line resolution of these isomers was achieved with a 299-ft QF-1 column (130 °C). The latter analysis showed that **6b** is not present in alkylation mixtures derived from **1-OAc** and **2-OAc**. Results of these experiments are included in Table I.

Alkylation Products. A. Alkylation with $LiCuMe_2$. Authentic samples of (*E*)- and (*Z*)-3-methyl-1-phenyl-1-butene (**3a** and **4a**) were obtained as follows. A binary mixture of these isomers was prepared by the Wittig reaction of benzylidenetriphenylphosphorane[17] and isobutyraldehyde, and samples of the isomers were separated from the mixture by preparative GC (5-ft column, 24% SF-96 on Chromosorb P, 30–60 mesh, 155 °C). The homogeneity of the samples was established by capillary GC (94-ft column, UCON LB 550X, 125 °C).

(*E*)-3-Methyl-1-phenyl-1-butene (3a) had the following: IR (neat) 3070, 3050, 3010, 2950, 2860, 1650, 1590, 1570, 1490, 1455, 1440, 1375, 1355, 1315, 1250, 1200, 1160, 1090, 1065, 1020, 960, 900, 830, 730, 680 cm^{-1}; UV (heptane) λ_{max} 251 nm (log ϵ 4.2), 284

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(3.2), 291 (2.9) [lit.[5] 251 (4.2), 284 (3.1), 293 (2.9)]; NMR ($CDCl_3$) δ 7.4–7.0 (m, 5 H), 6.45–5.9 (m, 2 H), 2.65–2.25 (m, 1 H), 1.08 (d, 6 H, J = 6 Hz). This sample had the same spectral properties and GC retention times as the major component of the alkylation product obtained with $LiCuMe_2$.

(*Z*)-3-Methyl-1-phenyl-1-butene (4a), isolated from the Wittig product, had the following: IR (neat) 3070, 3050, 3020, 3000, 2960, 2920, 2860, 1600, 1570, 1490, 1460, 1450, 1440, 1400, 1370, 1355, 1290, 1155, 1095, 1065, 1020, 920, 905, 850, 780, 750, 720, 700 cm^{-1}; UV (heptane) λ_{max} 241 nm (log ϵ 4.1), 291 (2.3) [lit.[5] 242 (4 .1), 291 (2.1)]; NMR ($CDCl_3$) δ 7.4–7.0 (m, 5 H), 6.3 (d, 1 H, J = 11 Hz), 5.5 (dd, 1 H, J = 11, 11 Hz), 3.1–2.7 (m, 1 H), 1.05 (d, 6 H, J = 6 Hz). This material had the same GC retention time as the minor component in the alkylation product obtained with $LiCuMe_2$.

(*E*)- and (*Z*)-4-Phenyl-2-pentene (5a and 6a) were obtained as a mixture from the Wittig reaction of ethylidenetriphenylphosphorane[17] and 2-phenylpropionaldehyde (Aldrich). Preparative GC (5-ft column, 24% SF-96 on Chromosorb P, 155 °C) gave a pure binary mixture shown by capillary GC (94-ft, UCON LB 550X, 90 °C) to be an 88:12 mixture of **6a** and **5a** (mixture A).[25] This binary mixture could not be separated by preparative GC. An analytical sample was prepared by column chromatography (silica gel, pentane) followed by Kugelrohr distillation. High-resolution mass spectrum: calcd for $C_{11}H_{14}$ m/e 146.10980, found m/e 146.10979. Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.38; H, 9.58.

A binary mixture consisting of 84% (*E*)-4-phenyl-2-pentene (**5a**) and 16% (*Z*)-3-methyl-1-phenyl-1-butene (**4a**) (mixture B) was isolated from the alkylation product of 1-OAc and $LiCuMe_2$ by preparative GC (above preparative column, 120 °C).

A 270-MHz NMR spectrum of mixture B (84% **5a**, 16% **4a**) showed that **(*E*)-4-phenyl-2-pentene (5a)** had the following: NMR ($CDCl_3$) δ 7.38–7.12 (m, 5 H), 5.60 (ddq, 1 H, J = 15.2, 6.6, 1.5 Hz), 5.44 (dqd, 1 H, J = 15.2, 6.1, 1.1 Hz), 3.40 (m, 1 H), 1.67 (ddd, 3 H, J = 6.1, 1.5, 1.1 Hz), 1.33 (d, 3 H, J = 7.0 Hz). Absorption due to the contaminant, **4a**, was determined from the spectrum for the latter.

Similarly the 270-MHz spectrum of mixture A (86% **6a**, 14% **15a**), corrected for the presence of **5a**, showed that **(*Z*-4-phenyl-2-pentene (6a)** had the following: NMR ($CDCl_3$) δ 7.4–7.0 (m, 5 H), 5.50 (m, 2 H), 3.78 (m, 1 H), 1.66 (d, 3 H, J = 6.4 Hz), 1.31 (d, 3 H, J = 7.0 Hz). The vinyl proton absorptions centered at δ 5.50 were simplified by irradiation of the vinyl methyl (C_1) protons. The C_3 proton signal collapsed to a doublet of doublets δ 5.53 (J = 10.5, 8.8 Hz), and the C_2 proton signal collapsed to a doublet, δ 5.44 (J = 10.5 Hz).

Low-pressure catalytic hydrogenation of mixture A (10% Pd on C) in ethyl acetate gave a single hydrogenation product, presumably 2-phenylpentane. Similarly, reduction of mixture B gave a binary mixture consisting of 84% of this same product together with 16% of an isomer, presumably 1-phenyl-3-methylbutane.

The minor component in mixture A had the same spectral properties and GC retention times as the major component in mixture B. The major component in mixture A (**6a**) was not detected in the $LiCuMe_2$ alkylation products.

B. Alkylation with LiCu(*n*-Bu)$_2$. Authentic samples of (*E*)- and (*Z*)-3-methyl-1-phenyl-1-heptene (**3b** and **4b**) were obtained as follows. A binary mixture of **3b** and **4b**, bp 91.5–94 °C (1.8 mm), was prepared by the Wittig reaction of benzyltriphenylphosphonium chloride[17] and 2-methylhexanal, using a standard procedure.[6] Capillary GC (94-ft column, UCON LB 550X, 130 °C) showed the composition to be 86% **3b** and 14% **4b**. Homogeneous samples of the olefins were obtained by preparative GC (10-ft column, 30% UCON on Chromosorb P, 130 °C).

(*E*)-3-Methyl-1-phenyl-1-heptene (3b) had the following: IR (neat) 3073, 3056, 3019, 2955, 2923, 2868, 2853, 1596, 1491, 1466, 1458, 1448, 1376, 983, 968, 753, 698 cm^{-1}; UV (pentane) λ_{max} 244 nm (log ϵ 4.1); NMR (CCl_4) δ 7.80–6.90 (m, 5 H), 6.18 (d, 1 H, J = 17 Hz), 5.88 (dd, 1 H, J = 8.0, 17 Hz), 2.22 (m, 1 H), 2.00–1.16 (m, 6 H), 1.03 (d, 3 H, J = 7 Hz), 0.98–0.78 (m, 3 H). Anal. Calcd for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found C, 89.33; H, 10.63. This sample had the same spectral properties and GC retention times as the major component of the alkylation product obtained with $LiCu(n\text{-}Bu)_2$.

(*Z*)-3-Methyl-1-phenyl-1-heptene (4b) had the following: IR (neat) 3070, 3050, 3025, 2990, 2950, 2920, 2865, 2850, 1491, 1465, 1458, 1449, 915, 799, 789, 765, 700 cm^{-1}; NMR (CCl_4) δ 7.16 (s, 5 H), 6.31 (d, 1 H, J = 11.6 Hz), 5.37 (t, 1 H, J = 11.6 Hz), 2.69 (m, 1 H), 1.26 (br s, 6 H), 1.03 (d, 3 H, J = 6.2 Hz), 0.69–0.95 (m, 3 H). Anal. Calcd for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.45; H, 10.24. This material had the same GC retention time as the minor component in the alkylation product obtained with $LiCu(n\text{-}Bu)_2$.

(*E*)- and (*Z*)-4-Phenyl-2-octene (5b and 6b) were obtained in 71% yield as a binary mixture from the Wittig reaction[6] of ethyltriphenylphosphonium iodide and 2-phenylhexanal.[26] The mixture was purified by column chromatography (silica gel, ether/pentane = 0.1) followed by vacuum distillation, bp 79–82 °C (1.5 mm). The composition of this mixture (mixture A′) was shown to be 69% **6b** and 31% **5b** by capillary GC (300-ft column, QF-1, 130 °C). Attempts to separate this mixture by preparative GC were unsuccessful.

In work to be reported elsewhere[8] it has been found that alkylation of 1-OAc with $LiCu(CN)n\text{-}Bu$ gives mixtures rich in **5b**. A pure binary mixture of 76% **5b** and 24% **6b** (mixture B′) was isolated from this alkylation product by preparative GC (10-ft column, 30% UCON on Chromosorb P, 130 °C). This mixture had the following: NMR (CCl_4) δ 7.46–6.80 (m, 5 H), 5.48 (m, 2 H), 3.55 (br q, 0.2 H, J = 8.5 Hz), 3.14 (br q, 0.8 H, J = 7 Hz), 1.66 (d, 3 H, J = 6 Hz), 1.52–1.07 (m, 6 H), 1.07–0.60 (m, 3 H).[10] Anal. Calcd for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.28; H, 10.70.

The vinyl proton absorptions in 270-MHz NMR spectra ($CDCl_3$) of mixtures A′ and B′ were simplified by irradiation of the vinyl methyl (C_1) protons.[27] These spectra showed that **(*Z*)-4-phenyl-2-octene (6b)**, the major component of mixture A′, had vinyl proton absorption centered at δ 5.54 (C_3 proton, dd, J = 10.7, 8.3 Hz) and δ 5.48 (C_2 proton, d, J = 10.7 Hz). The vinyl proton absorptions for **(*E*)-4-phenyl-2-octene**, the major component in mixture B′, are centered at δ 5.57 (C_3 proton, dd, J = 15.2, 7.5 Hz) and δ 5.42 (C_2 proton, d, J = 15.2 Hz).

The spectral properties and GC retention time of the minor component in mixture A′ were indistinguishable from those for the major component in mixture B′ and vice versa. The major component in A′, **6b**, was not detected in products resulting from alkylation of 1-OAc or 2-OAc with $LiCu(n\text{-}Bu)_2$.

Diimide reduction[28] of mixtures A′ and B′ gave a single product, 4-phenyloctane, which had the same spectral properties and GC retention time as an authentic sample prepared by alkylation of 1-bromo-1-phenylbutane[29] with $LiCu(n\text{-}Bu)_2$, using a general procedure.[30] All samples of *dl*-4-phenyloctane had the same spectral properties as an authentic sample of optically active 4-phenyloctane.[26]

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Registry No. (*E*)-1-OH, 36004-04-3; (*E*)-1-OAc, 74457-38-8; (*E*)-1-OTMS, 76987-16-1; (*E*)-2-OH, 52755-39-2; (*E*)-2-OAc, 79594-08-4; (*E*)-2-OTMS, 79594-09-5; (*E*)-**3a**, 15325-61-8; (*E*)-**3b**, 79594-10-8; (*Z*)-**4a**, 15325-56-1; (*Z*)-**4b**, 79594-11-9; (*E*)-**5a**, 42461-65-4; (*E*)-**5b**, 79594-12-0; (*Z*)-**6a**, 76807-04-0; (*Z*)-**6b**, 79594-13-1; (*E*)-1-phenyl-1-pentene, 16002-93-0; (*Z*)-1-phenyl-1-pentene, 7642-18-4; $LiCuMe_2$, 15681-48-8; $LiCu(n\text{-}Bu)_2$, 24406-16-4.

(25) The Schlosser–Christman Wittig procedure (ref 7) gave an 80:20 mixture of **6a** and **5a**.

(26) The preparation and characterization of this compound will be published elsewhere. Suitable spectral data and combustion analysis were obtained.

(27) We are indebted to Mr. Dominic M. T. Chan for providing us with these decoupled spectra.

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