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SOME UNUSUAL ASPECTS OF ORGANOCOPPER CHEMISTRY. LITHIUM ORGANOCUPRATE REACTION WITH SOME NEOPENTYLIC *p*-TOSYLATE ESTERS *

GARY H POSNER * and KEVIN A BABIAK

Department of Chemistry The Johns Hopkins University Baltimore Maryland 21218 (U S A)

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Summary

Diphenylcopperlithium and dimethylcopperlithium react differently with the same primary neopentylic tosylate ester Several secondary neopentylic tosylates react with organocopperlithium reagents to give olefins via a concerted anti-1,2-dehydrosulfonation When anti-elimination is not possible, skeletal rearrangement occurs

In the field of organometallic chemistry, organocopper reagents have enjoyed widespread acceptance and use during the past ten years [1] Two major reasons for the current phenomenal importance of organocopper reagents are their ease of preparation and their selectivity toward one type of functional group in complex polyfunctional molecules Addition of organocopper reagents to carbon—carbon multiple bonds [2] and organocopper substitution reactions with carbon electrophiles [3] have been applied successfully in the crucial step of a great many synthetic transformations, including syntheses of many natural products

Alkyl sulfonate esters have been used often as carbon electrophiles in organocopper substitution reactions leading reliably, reproducibly, and efficiently to linkage of two different hydrocarbon groups even when the groups are bulky [4] Johnson has shown, for example, that even classically unreactive and sterically hindered neopentyl *p*-tosylate undergoes displacement by a phenyl group when exposed to diphenylcopperlithium [4]. We report here our observation on the unusual and sharp difference in behavior between diphenyl- and dimethyl-copperlithium toward the same primary neopentylic tosylate and also on the unexpected dehydrosulfonation and skeletal rearrangement of some secondary neopentylic tosylates when exposed to diorganocopperlithium reagents

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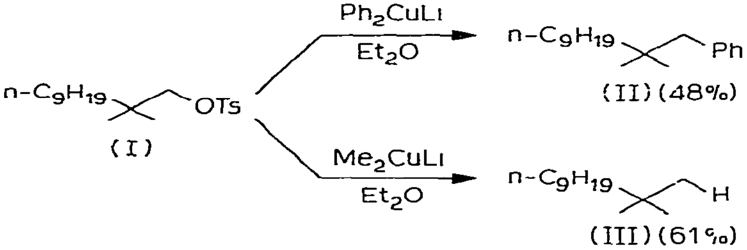
* Dedicated to Professor H Normant on the occasion of his 72nd Birthday

Primary neopentylic tosylate I underwent displacement by diphenylcopperlithium as expected to form hydrocarbon II (eq 1) In sharp contrast, the same tosylate I underwent reduction by dimethylcopperlithium to form hydrocarbon III β-Elimination of copper hydride [5] from an intermediate organocopper species is impossible in this case because there are no β-hydrogens Quenching the reaction with D_2O gave only hydrocarbon III, with no deuterium incorporation which indicated the absence of any long-lived neopentylic copper species. Although a neopentyl radical is a possible intermediate which could abstract a hydrogen atom from the ethereal solvent, Whitesides has shown in a similar case that dineophylcopperlithium undergoes oxidative dimerization without any phenyl migration (i e skeletal rearrangement) characteristic of neophyl (2-phenyl-2-methyl-1-propyl) radicals [6] Therefore the mechanism for conversion of tosylate I to reduced hydrocarbon III remain puzzling.



(1)

Johnson has suggested that formation of olefins often as minor by-products when secondary tosylate esters are exposed to organocopper reagents occurs via a concerted E_2 process [4]. To test the generality and concertedness of this elimination (i.e., dehydrosulfonation) process, we have examined the reactions of various secondary neopentylic tosylates with lithium organocuprates A concerted 1,2-elimination should give skeletally unrearranged products, and substitution should predominate over elimination especially for acyclic systems. Our results are summarized in Table 1

Acyclic neopentylic tosylates IV and V were dehydrosulfonated cleanly forming the corresponding t-butylalkenes; no substitution products were detected!

Mechanistic interpretation of the results in Table 1 is difficult Although transient copper(III) intermediates have been invoked often in discussion of organocopper substitution reactions [1—3,7], our failure to detect any copper hydride (from β-elimination leading to olefin) or any R—H (from CuH reduction [6] of R—OTs) in these secondary neopentylic systems prompts us to interpret reactions of tosylates IV—VI as concerted * 1,2-eliminations Presumably the congestion about the neopentylic carbon atom prevents replacement of the tosyloxy group by copper and directs the course of the reaction toward elimination (i.e. dehydrosulfonation) rather than toward the expected substitution.

These β-eliminations of tosylates IV—VI must be concerted processes because

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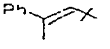
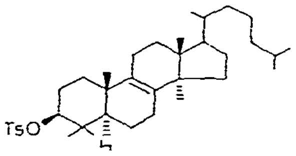
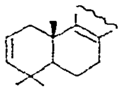
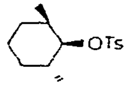
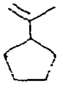
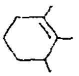
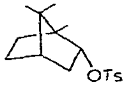
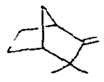
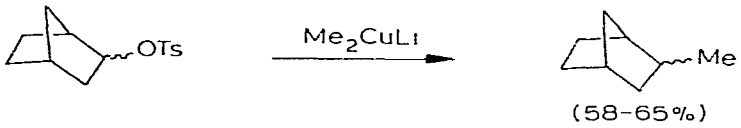
* Concerted is not meant to imply anything about the relative extent of C_β-H and C_α-OTs bond breaking in the transition state.

TABLE 1

DEHYDROSULFONATION OF SOME SECONDARY NEOPENTYLIC TOSYLATES USING DIORGANOCOPPERLITHIUM REAGENTS

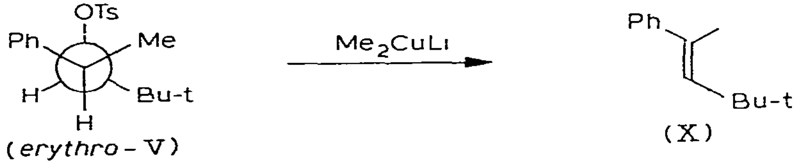
Secondary neopentylic p-tosylates	R in R_2CuLi	Major product (Yield %)	
$n\text{-}C_9H_{19}CH(OTs)C_4H_9\text{-}t$ (IV)	Me	$n\text{-}C_8H_{17}CH\overset{t}{=}CHC_4H_9\text{-}t$ (IX)	(77)
IV	Ph	IX	(80)
erythro-$C_6H_5CH(CH_3)CH(OTs)C_4H_9\text{-}t$ (V)	Me	 (X)	(80)
 (VI)	Me	 (XI)	(64)
VI	Ph	XI	(32)
 (VII)	Me	 (XII)	(33)
		 (XIII)	(27)
 (VIII)	Me	 (XIV)	(63)
VIII	Ph	XIV	(60)

no skeletally rearranged products were formed, even in the case of steroidal neopentylic tosylate VI which has a pronounced tendency to undergo carbonium ion initiated Wagner—Meerwein alkyl shifts at the very slightest provocation and under very mild conditions [8] The lithium cuprates must therefore be assisting loss of the tosylate group by acting as a Lewis acid [9] and also at the same time must be participating in abstraction of a proton from the β-carbon atom This cooperative pull—push mechanism seems likely because the cuprates are not sufficiently basic to initiate the β-elimination by abstraction of a proton from an unactivated carbon atom [1—3], and a step-wise process starting with tosylate ionization would have led to carbonium ion rearrangements This concerted dehydrosulfonation proceeds via loss of *trans*-oriented hydrogen and sulfonate groups, when such a *trans*-relationship is absent, as in cyclohexyl tosylate VII, then dehydrosulfonation proceeds with skeletal rearrangement. Likewise, bornyl tosylate VIII, having only a β-H—tosylate *cis*-relationship, underwent a 1,3-elimination with a skeletal reorganization rather than a direct *cis*-1,2-elimination. This elimination of *p*-tosic acid from bornyl tosylate VIII stands in sharp contrast to the substitution of norbornyl tosylate (eq. 2) [4].

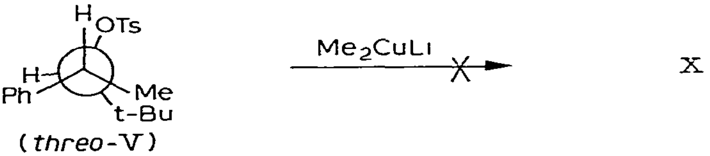


(2)

This tendency toward *trans*-1,2-elimination is very strong. Although acyclic *erythro*-V can adopt a suitable conformation for *trans*-dehydrosulfonation (eq. 3), *threo*-V cannot and therefore it undergoes dehydrosulfonation to give a mixture of 4 major products (some of which must be skeletally rearranged). Apparently, *syn*-elimination from the conformer of *threo*-V shown below is not the major reaction pathway (eq. 4).



(3)



(4)

In conclusion, the unusual and unexpected aspects of organocopper chemistry reported here serve to alert the chemical community to some major "side-reactions" which can occur when organocopper reagents are used with the intention of effecting substitution reactions on neopentylic tosylates.

Experimental

Elemental analyses were performed by Chemalytics, Inc., Tempe, Arizona. Melting points are uncorrected and were performed on Thomas—Hoover Melt Temp. Mass spectra were performed on a Hitachi—Perkin—Elmer MU-6 at an ionizing voltage of 70 eV. Infrared spectra were recorded as solutions in carbon tetrachloride (CCl_4) or chloroform ($CDCl_3$) on a Perkin—Elmer 337 spectrophotometer and all recorded absorptions were corrected by reference to the polystyrene band at 1601 cm^{-1}. PMR spectra were obtained on a Varian A-60A or JEOL MH-100 spectrophotometer with CCl_4 or $CDCl_3$ as solvent and all spectra were standardized vs. tetramethylsilane (TMS). Preparative VPC separations were obtained with a Varian Aerograph Model 90-P instrument equipped with thermal conductivity detector and He as the carrier gas. Analytical VPC determinations were measured using a Varian Aerograph Model 1200 instrument with flame ionization detector and He as carrier gas. Quantitative VPC yield determinations resulted from integration of peak areas vs. added internal standards with concomitant calibration of detector response factors. The VPC columns used are identified as column A: $10' \times \frac{1}{8}''$ 5% SE-30 on 100—140 mesh Chrom G, Flow rate 20 cm^3 He/min, column B. $10' \times \frac{1}{8}''$ % Carbowax 20M on

60—80 mesh Chrom W Flow rate 20 cm^3 He/min, (preparative) Column C 10 × ¼′ 20% SE-30 on 40—60 mesh Chrom W Flow rate 60 cm^3 He/min PMR yield determinations were accomplished by integration of pertinent PMR signals vs the signal due to a known amount of added internal standard (usually trichloroethylene [TCE])

All solvents were reagent grade Anhydrous ether and tetrahydrofuran were distilled from benzophenone ketyl under N_2 Anhydrous pyridine was distilled from CaH_2 under N_2

Cuprous iodide and cuprous bromide (Fisher Chem Co) were continuously extracted with THF

Reaction of tosylate I with dimethylcopperlithium

To a 50 ml 2-necked round-bottom flask equipped with magnetic stirrer and serum stopper was introduced 1 90 g (10 0 mmol) of cuprous iodide The flask was then heated gently with a microburner to drive residual water out while the flask was purged with N_2 The serum stopper was replaced by a three-way stopcock carrying a nitrogen-filled balloon and a positive pressure of N_2 was maintained throughout the reaction To the cooled flask (0° C) was added 10 ml of anhydrous Et_2O and to it was added via syringe 16 7 ml (20 0 mmol) of 1 20 M methyllithium in Et_2O (just faint yellow color of methylcopper precipitate remained) The reaction was stirred at 0° C for 15 min and then a solution of 340 mg (1 0 mmol) of tosylate I in 5 0 ml of anhydrous Et_2O was added via syringe The mixture was stirred at 0° C for 1 h and then at room temperature for 48 h During this time the reaction went from clear and nearly colorless to one of a yellow precipitate and finally to a black precipitate Thin layer chromatography (TLC) on silica with 10% Et_2O/benzene showed no starting material present (a single hydrocarbon component at high R_f) The reaction mixture was quenched by pouring it into a 50 ml of saturated NH_4Cl together with a 40 ml of Et_2O as rinse The two phase mixture was stirred at room temperature for 1 h and the Et_2O layer separated The aqueous layer was extracted twice with 30 ml of Et_2O and the combined extracts were dried over anhydrous $MgSO_4$ Solvent was removed at reduced pressure to give yellow oil PMR analysis (CCl_4) showed only normal aliphatic signals and complete absence of resonances due to starting material VPC analysis (column A, 115° C) vs 59 4 mg of undecane gave a 60 6% yield of a single major component III Preparative VPC (column C, 130° C) provided a clear colorless oil IR (CCl_4) gave signals characteristic of a hydrocarbon The presence of a t-butyl group is evident by characteristic bands at 1255 and 1210 cm^{-1} and the strong *gem*-dimethyl doublet at 1380 cm^{-1} The mass spectrum showed an $M - 1$ peak at m/e 169 and a strong, $M - 16$ peak at 154 m/e PMR (CCl_4) showed a strong singlet at δ 0 80 ppm indicative of a t-butyl group

Reaction of tosylate I with dimethylcopperlithium and subsequent D_2O quench

The general procedure as described above was followed for 3 days reaction time, followed by quenching the reaction with D_2O for 1 h, followed by saturated NH_4Cl and standard work up Again, VPC analysis (column A, 115° C) showed only one major component III Preparative VPC (column C, 130° C) gave a clear oil identical in all respects with that previously prepared including the mass spectrum which showed no deuterium incorporation

Reaction of tosylate I with diphenylcopperlithium

As above 430 mg (3.0 mmol) of cuprous bromide in 10 ml of anhydrous Et_2O at 0° C was treated with 4.2 ml (6.0 mmol) of 1.34 *M* phenyllithium in benzene/ether for 15 min. The solution was pale green. To this was added via a syringe 340 mg (1.0 mmol) of tosylate I in 7.0 ml of anhydrous Et_2O. The reaction was stirred at 0° C for 30 min and at room temperature for 24 h. TLC analysis (on silica with 10% ether/benzene) of an aliquot removed after 24 h showed that no starting material remained and that in addition to a high R_f material much biphenyl was also present. Work up as before provided 0.91 g of a yellow oil. VPC analysis (column A, temp programmed 120—220° C) of the reaction residue vs. 54.3 mg of dodecane showed only one major product II in a 48% yield. Preparative VPC (column C, ~150° C doubly collected) gave a clear oil. PMR (CCl_4) δ 7.1 ((br)m, ArH, 5), 2.45 (s, CH_2—Ar, 2 H) 2.0—0.6 ((br)m, skeletal H, 17 H) and 0.83 (s, *gem* di-CH_3, 6 H) ppm, IR (CCl_4) 3090, 3080, 3030, 2920, 2850, 1600, 1490, 1465, 1450, 1380, 1360, 1170, 1065, 1025, 715, 695 cm^{-1}. Mass spectrum gave a molecular ion at *m/e* 246 and a base peak at *m/e* 155 [$M - C_7H_7$]. Analysis Found C, 87.18, H, 12.11. $C_{18}H_{30}$ calcd C, 87.73; H, 12.27%.

Reaction of tosylate IV with dimethylcopperlithium

As above 368 mg (1.0 mmol) of IV was allowed to react with 3.0 mmol dimethylcopperlithium at 0° C for ~2 h and then at +5° C in a cold room for total reaction time of 24 h. TLC of an aliquot at this time on silica with 10% ether/benzene showed no starting material. Usual workup provided 218 mg of an oil. VPC analysis (column A, 135° C) showed one major component, (*E*)-2,2-dimethyl-3-dodecene (IX), in 77% yield and one unidentified minor compound (~7%) vs. 58.0 mg dodecane as an added internal standard. VPC collection (2×) (column C, 160° C) provided ~100 mg of a clear colorless oil. PMR (CCl_4) δ 5.33 (t, vinyl-H, 2 H, *J* ~2 Hz), 2.2—0.5 ((br)m, skeletal-H, 17 H), 1.00 (s, t-butyl, 9 H) ppm; IR (CCl_4) 3000, 2950, 2915, 2850, 1460, 1390, 1375, 1360, 1265, 1200, 1020, 965 (*trans* double bond), 710 cm^{-1}. The mass spectrum showed a strong molecular ion at *m/e* 196. Analysis Found C, 85.78, H, 14.63. $C_{14}H_{28}$ calcd : C, 85.63, H, 14.45%.

Reaction of tosylate IV with diphenylcopperlithium

As above, 184 mg (0.5 mmol) of IV was allowed to react with 1.5 mmol of diphenylcopperlithium at 0° C for 30 min and then at room temperature for 48 h. Normal workup provided a yellow oil which was mostly biphenyl. PMR analysis (CCl_4) showed only one non-aromatic olefinic signal which could be attributed to IX. VPC analysis (column A, 140° C) vs. 73.4 mg dodecane indicated IX was formed to the extent of 80%. VPC collection (column C, 140° C) gave a product identical to IX prepared above.

Reaction of 2-phenylpropionaldehyde with t-butyllithium to give erythro-2-phenyl-4,4-dimethyl-3-pentanol (V)

Into a 3 necked 250 ml flask equipped with magnetic stirrer, equilibrium armed addition funnel and serum stopper was introduced 13.4 g (0.1 mol) of distilled 2-phenylpropionaldehyde and 75 ml of anhydrous ether. The reaction flask was cooled to —78°C and to it was added 81 0 ml (0 15 mol) 1 86 *M* t-butyllithium in pentane dropwise over 30 min The reaction was then stirred at —78°C for 1 h, overnight at room temperature and quenched by dropwise addition of H_2O (50 ml) The organic layer was separated and the aqueous layer extracted twice with 50 ml of ether The combined ether extracts were dried ($MgSO_4$) and concentrated at reduced pressure Short path distillation (83—98°C at 0 8 mmHg) provided 12 62 g (66%) of a clear oil VPC analysis (column A, 150°C) showed a 9/1 ratio of *erythro/threo* alcohols [10]. PMR (CCl_4) δ 7.13 ((br)m, ArH, 5 H), 3 31 (d, CHOH, 1 H, J ~3 5 Hz) 2 93 (dq, CHAr, 1 H, J 7 0 Hz, 4 0 Hz) 1 24 (d, CH_3CH, 3 H, J 7 0 Hz), 0 90 (s, t-butyl, 9 H) ppm, IR (CCl_4) 3640, 3090, 3070, 3030, 2960, 2870, 1600, 1495, 1480, 1470, 1455, 1395, 1385, 1365, 1090, 1025, 995, 970, 700 cm^{-1}

Formation of erythro-2-phenyl-4,4-dimethyl-3-pentyl tosylate (V)

In a procedure identical to that for the preparation of tosylate VII, 2 88 g (15 mmol) of parent alcohol (as a 90/10 *erythro/threo* mixture) in 10 ml of anhydrous pyridine was allowed to react with 3 80 g (20 mmol) recrystallized tosyl chloride for 4 days at room temperature, TLC (10% ethyl acetate/benzene on silica gel) showed no starting material and two products PMR analysis (CCl_4) after standard workup showed that in addition to the expected CHOTs proton signal at δ 4.65 ppm, an olefin signal appeared at δ 5 63 ppm The crude residue was recrystallized from 2/1 ether/hexane at —10°C to give 0 76 g (15%) of white needles (m p 69 0—69 5°C, dec) PMR (CCl_4) δ 7 4 (AA'BB'q, Ar, H, 4 H), 7 1 ((br)s, unsubst ArH, 5 H) 4 63 (d, CHOTs, 1 H, J 2 Hz), 3 08 (dq, CHO, 1 H, J 6 0 and 2 5 Hz), 2 40 (s, $ArCH_3$, 3 H), 1 31 (d, CH_3-CHPh, 3 H, J ~7 0 Hz), 0.85 (s, t-butyl, 9 H) ppm, IR (CCl_4) 3060, 3030, 2960, 2870, 1600, 1495, 1480, 1450, 1400, 1360, 1305, 1290, 1185, 1175, 1095, 1045, 1025, 1015, 910, 845, 700, 675 cm^{-1} Analysis Found. C, 69 20, H, 7 52, S, 9 31 $C_{20}H_{26}O_3S$ calcd C, 69 33, H, 7 56, S, 9 26%

Reaction of tosylate V with dimethylcopperlithium

As above, 107 mg (0 31 mmol) of tosylate V was allowed to react with 3 30 mmol of dimethylcopperlithium at 0°C for 1 h and at room temperature for 48 h No starting material remained by TLC Standard workup was followed by concentration of the dried ethereal extracts at atmospheric pressure through a 20 m vigreux column VPC analysis (column A, temp program from 70 to 150°C) showed a single major product (X) in 68% yield vs 43 5 mg of n-nonane Preparative VPC (column C, 135°C) provided pure X as a clear oil PMR (CCl_4) δ 7 1 (bm, ArH), 5 33 (m, vinyl H), 1 90 (d, allylic CH_3), 0 82 (s, t-butyl) ppm, IR (CCl_4) 3080, 3030, 2950, 1600, 1500, 1475, 1465, 1450, 1435, 1400, 1370, 1230, 1190, 1075, 1030, 920, 705 cm^{-1}.

The *E*-geometry of olefin X was assigned mainly on the basis of the characteristic chemical shift of the allylic methyl group (δ 1 9 ppm) as compared to its chemical shift in *E*-2-phenyl-2-butene (δ 1 85 ppm) and in *Z*-2-phenyl-2-butene (δ 1.45 ppm) [11] The mass spectrum showed a parent peak at *m/e* 174°, exact *m/e*· 174 141, $C_{13}H_{18}$calcd 174.140

Reaction of lanosteryl tosylate VI with dimethylcopperlithium

As above, 291 mg (0 5 mmol) of tosylate VI was allowed to react with 1 5 mmol of dimethylcopperlithium at 0° C for 15 min and then at the reflux temperature of ether for 48 h TLC on silica gel with 10% ether benzene showed no starting material Usual workup gave 261 mg of a crude oil PMR analysis (CCl_4) of the crude product vs 160 0 mg of TCF indicated a 64% yield of olefin XI (δ 5.10 ppm vinyl H), identical with that of an authentic sample [12] and a trace of unidentified material (δ 4 75 ppm) The crude product was sublimed three times (130° C, 0 2 mmHg) to give a waxy solid m p 60 0—66 0° C The mass spectrum showed a molecular ion at *m/e* 110

Preparation of trans-2,2,6-trimethylcyclohexyl tosylate (VII)

In an oven dried flask was placed 0 89 g (6 26 mmol) of *trans*-2,2 6-trimethylcyclohexanol (m p 14 5—48 5° C) along with 7 ml of anhydrous pyridine and 2 38 g (12.52 mmol) of recrystallized *p*-toluenesulfonyl chloride The reaction mixture was swirled to attain homogeneity, protected from atmospheric moisture with a drying tube and allowed to stand for 4 days at room temperature at which point a heavy precipitate of pyridinium hydrochloride had formed The reaction mixture was then poured into ice cold 1 *N* HCl and extracted three times with 30 ml of ether The combined ether extracts were then stirred together with ~100 ml 2% diethylenetriamine for 2 h to remove excess tosyl chloride. The organic layer was separated and washed once with 30 ml of 1 *N* HCl, 30 ml of saturated $NaHCO_3$ and 30 ml of saturated NaCl and dried over anhydrous $MgSO_4$ Removal of solvent at reduced pressure gave ~1 8 g of a crude solid (m p 63 0° C, dec) One recrystallization from hexane gave 1 69 g (91%) of VII as a white crystalline product An analytical sample was obtained by two further recrystallizations from hexane (m p 69 0° C dec) PMR (CCl_4) δ 7 45 (AA'BB' *q*, ArH, 4 H), 4.08 (d, CHOTs, 1 H, *J* 9 8 Hz), 2 42 (s, $ArCH_3$, 3 H), 2 1—0 5 ((br)m, ring proton, 7 H), 0 87 (s, 3-CH_3, 9 H) ppm, IR (CCl_4) 2940, 2870, 2850, 1600, 1460, 1360, 1305, 1290, 1210, 1187, 1177, 1090, 925, 890, 870, 670 cm^{-1}. The mass spectrum showed only [*M* — HOTs] at 124 *m/e*.

Reaction of tosylate VII with dimethylcopperlithium

As above, 296.0 mg (1 0 mmol) of tosylate VII was treated with 3 0 mmol of dimethylcopperlithium at 0° C for 48 h. The usual workup provided an ethereal solution which was concentrated at atmospheric pressure by distillation through a 20 cm vigreux column VPC analysis (column A, 80° C) vs 51 4 mg of undecane as internal standard provided the following product distribution (overall yield 85.1%) A, 9 0 min retention time, 10.7%, B, 10 2 min, 24 5%, C, 11 5 min, 33.4%; D, 16 5 min, 26 9%, E, 22.3 min, 9 6% The components A, C, D, E were VPC collected (column C, 80° C). The mass spectrum indicated that A (*m/e* 126) was formed as a result of hydride replacement of tosylate, that C and D (*m/e* 124) were the result of loss of HOTs from VII and that E (*m/e* 140) resulted from displacement of OTs by CH_3. PMR (CCl_4) of C δ 4.60 (s, $=CH_2$), 1 60 (s, CH_3—C≡C) 0.9 ((br)d, CH_3—CH) and IR (CCl_4) 885 cm^{-1} indicate *trans*-1-methyl-2-isopropenylcyclopentane (XII), and PMR (CCl_4) of D δ 1.5 (s, $=CCH_3$, 6 H), 0 95 (d, 3 H) ppm indicate 1,2,3-trimethylcyclohexene.

Reaction of bornyl tosylate VIII with diphenylcopperlithium

As above, 308 mg (1 0 mmol) of the tosylate VIII was allowed to react with 3 0 mmol of diphenylcopperlithium initially at 0° C The reaction was then stirred at reflux for 48 h Usual workup gave an ethereal extract which was concentrated at atmospheric pressure by distillation using a 20 cm vigreux column VPC analysis (column A, 90° C programmed to 200° C) of the residue vs 50 3 mg of undecane provided a 60% yield of camphene XIV plus some other unidentified component Preparative VPC collection (column C, 100° C) gave a white waxy solid whose IR was identical to that displayed in Aldrich Infrared Library 32-A The mass spectrum showed a molecular ion at *m/e* 136

Reaction of tosylate VIII with dimethylcopperlithium

As above, 308 mg (1 0 mmol) of bornyl tosylate VIII was treated initially at 0° C with 3 mmol of dimethylcopperlithium and stirred at reflux for 48 h Workup as usual gave a concentrated ethereal solution VPC analysis (column A, 90° C) vs 65 6 mg dodecane showed 2 major products and 2 minor products The major products had retention times of 10 9 and 19 0 min vs 29 4 min for standard Integration provided 62 7% yield of XIV and 16 0% of monoalkylated material Preparative VPC collection (column C, 90° C) gave clear colorless oils The shorter retention time material was identical to camphene XIV by IR and by coinjection with an authentic sample on VPC The mass spectrum of the longer retention time material showed a molecular ion at *m/e* 152, IR showed no olefinic signals and only absorptions due to saturated hydrocarbon, the structural identification of this product was not pursued further

Acknowledgment

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