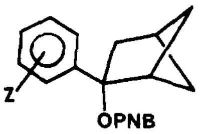
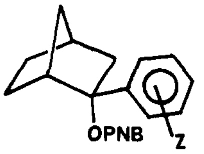
The system (**6**) reveals excellent log k-σ^+ relationship.[10] The aryl derivatives yield a value of ρ^+ -4.31 (correlation coefficient 0.999).

If the strained cyclobutane moiety facilitates solvolysis by σ-participation, ρ^+ in this system should be more positive than in the 2-aryl-*endo*-norbornyl derivatives (**7**). However, this is not observed. Indeed, ρ^+ is more negative, indicating the unimportance of σ-participation in this system.



6

-4.31



7

-3.72

The question next arises as to whether bridging can be absent in the tertiary derivatives examined, but present in the secondary. The observed rate of solvolysis for 2-bicyclo[2.1.1]hexyl tosylate (**1**) fails to exhibit any enhancement in rate attributable to σ-participation. Thus the rate of acetolysis for **1** is reported to be 1.7×10^{-5} s^{-1} at 75 °C.[11] This is three times slower than the rate for *endo*-norbornyl tosylate and 1000 times slower than that for *exo*-norbornyl tosylate, a molecule to which it is structurally related. With $\nu_{C=O}$ 1764 cm^{-1},[12] application of the Foote-Schleyer correlation does not reveal any enhanced rate attributable to significant σ-participation.[1,13] Finally, extrapolation of the data from tertiary 2-bicyclo[2.1.1]hexyl derivatives (**6**) to the secondary using the recently developed substituent constant for hydrogen[14] fails to reveal any enhanced rate for the secondary derivative attributable to the incursion of σ-participation (Figure 1). (The calculated value is 19.5×10^{-19} s^{-1}, as compared to the observed value, 7.33×10^{-19}.)

It is, of course, hazardous to extrapolate conclusions based on solvolytic data to stable ion conditions,[15] or to the gas phase[16] (and vice versa). However, with this reservation in mind, it is evident that our results and conclusions are in better agreement with the position reached by Olah[5] than with that of Wiberg[4] or of Dewar.[2]

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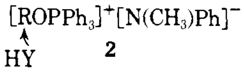
Direct Substitution of Hydroxyl Groups of Allyl Alcohols with Alkyl Groups by the Reaction of Lithium Allyloxyalkylcuprates with *N,N*-Methylphenylaminotriphenylphosphonium Iodide. Regio- and Stereoselective Olefin Synthesis

Sir:

The allylic unit[1] is a common structural feature of many compounds of natural origin, and the most important synthon for such units are allyl alcohols. We wish now to report a novel and efficient method for direct substitution of a hydroxyl group of alcohols with alkyl or aryl groups of the corresponding organolithium compounds in a single step as depicted in eq 1. The reaction appears to be general and particularly efficient for regio- and stereoselective synthesis of olefins from allyl alcohols.

$$R^1OH \xrightarrow[4.\ [Ph_3PN(CH_3)Ph]^+I^-\ (1)]{1.\ CH_3Li,\ 2.\ CuI,\ 3.\ R^2Li} R^1\text{-}R^2 \qquad (1)$$

N,N-Methylphenylaminotriphenylphosphonium iodide (**1**)[2] is a versatile reagent for regio- and stereoselective syntheses of amines and sulfides from alcohols. Nucleophilic attack of amines or sulfides toward a key intermediate of aminophosphonium salt (**2**) seems to proceed like an S_N2 type reaction.[3] When methylmetallic reagents such as methyllithium, methylcopper, and lithium dimethylcuprate were allowed to react with **2**, methylation products were obtained in less than 15% yield along with *N,N*-methylphenylamines (85-99%), indicating that the nucleophilic character of *N*-methylanilide toward the alkoxy group of **2** is stronger than that of the methyl



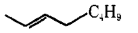
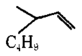
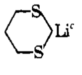
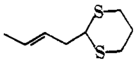
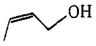
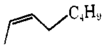
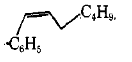
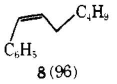
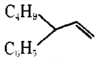
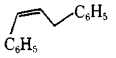
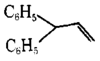
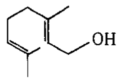
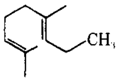
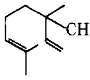
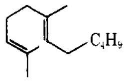
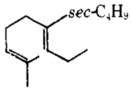
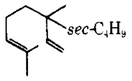
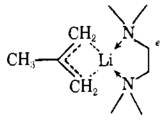
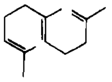
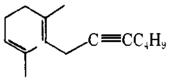
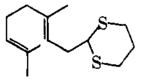
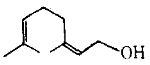
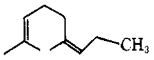
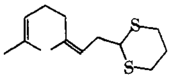
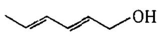
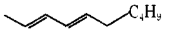
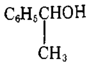
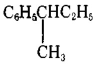
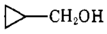
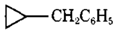
$$\underset{\overset{\uparrow}{HY}}{[R}OPPh_3]^+[N(CH_3)Ph]^- \quad \mathbf{2}$$

moiety. We chose to investigate mixed cuprates[4] as alkylating agents since we anticipated that *N*-methylanilide in the mixed cuprates bonds to copper tightly, and, consequently, inhibiting the nucleophilic attack toward the α-carbon of the alkoxy group. Indeed, the reaction of lithium geranylalkoxymethylcuprate with **1** gave methylation products, (**6E**)-2,6-dimethyl-2,6-nonadiene (**3**) and 3,3,7-trimethyl-1,7-octadiene (**4**) in 90% yield (**3**/**4** = 50/50); *N,N*-methylphenylgeranylamine was not present. High regioselectivity (**3**/**4** = 93/7) was obtained upon treatment with 3 equiv of methyllithium (entry 6)[5] Although the detailed structure of the alkylating reagents remains obscure, admixture of lithium alkoxylalkylcuprate and alkyllithium is presumably a bulky, highly reactive cuprate having the stoichiometry $R^1OCuR^2_3Li_3$ analogous to Me_3CuLi_2 or Me_4CuLi_3.[6]

Table I summarizes the representative examples. Alkylation and arylation proceed well (entries 1, 3-8, 12, 14-17) and require no comment except that secondary butyllithium provides the corresponding alkene without difficulty (entry 8).[1b] The versatility of the organolithium compounds evidently enhances the synthetic utility of the reaction. Thus, reaction of geranyl alcohols with methallyllithium (entry 9) or 1-hexynyllithium (entry 10) gave the corresponding 1,5-diene or 4-ene-1-yne, respectively, with complete regioselectivity. Further, reaction with a molar equivalent of 2-lithio-1,3-dithiane (entries 2, 11, 13) gave a valuable intermediate, 2-allyl-1,3-dithiane. Importantly, the substitution at the allylic position proceeds with inversion of configuration. Thus, reaction of *trans*-4-*tert*-butyl-2-cyclohexen-1-ol[7] (*trans*-**5**) with methyllithium under the present reaction conditions gave *cis*-3-*tert*-butyl-6-methyl-1-cyclohexene[8] (**6**) stereoselectively in 75% isolated yield (entry 15).[9]

Naturally, simple alcohols can be converted into hydrocarbons in high yields. Thus, α-methylbenzyl alcohol and cyclopropylcarbinol can be converted into 2-phenylbutane (65%

Table I. Alkylation and Arylation of Alcohols[a]

Entry	Substrate	Alkylating agent[b]	Products[f] (relative ratio, %[g])		Bp (°C/mmHg)	Isolated yield, %[i]
1		n-C_4H_9Li	 (91)	 11(9)	–	80[j]
2		 [c]	 (99)	—	160/2[h]	78
3		n-C_4H_9Li	 (96)	11 (4)	–	73[j]
4		n-C_4H_9Li	 8(96)	 9(4)		80
5		C_6H_5Li	 (76)	 (24)	125–130/4	72
6		CH_3Li	 3(93)	 4(7)	81–84/30	90
7		n-C_4H_9Li	 (99)	—	86–90/15	92
8		sec-C_4H_9Li	 (96)	 (4)	120/19[h]	90
9		 [e]	 (99)	—	–	90[j]
10		n-$C_4H_9C\equiv CLi$	 (99)	—	–	84[j]
11			 (99)	—	200/2[h]	76
12		CH_3Li	 (92)	4 (8)	76–80/30	81
13			 (99)	—	200/2[h]	73
14		n-C_4H_9Li[c]	 (99)	—	45–47/38	81
15	*trans*-5	CH_3Li[d]	*cis*-6 (99)	—	90–92/40	75
16	 $C_6H_5CH(OH)CH_3$	C_2H_5Li[c]	 $C_6H_5CH(CH_3)C_2H_5$		–	65[k]
17		C_6H_5Li[c]			42–45/100	73

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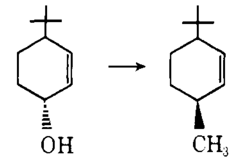
[a] Alkylation was carried out under the same reaction condition as described about a representative case. [b] Three molar equivalents of organolithium was utilized unless otherwise indicated. [c] One molar equivalent of organolithium was utilized. [d] Two molar equivalents of CH_3Li was utilized. [e] S. Akiyama and J. Hooz, *Tetrahedron Lett.*, 4115 (1973). [f] All products exhibited satisfactory spectral and analytical data. [g] Determined by GLC. [h] Bulb-to-bulb distillation. [i] Isolated yields by reduced distillation unless otherwise indicated. [j] By preparative TLC (silica gel). [k] By column chromatography (silica gel).



5 → 6 (75%)

isolated yield)(entry 16) and cyclopropylphenylmethane (73%) (entry 17), respectively, upon treatment with the corresponding organolithium compounds under the same reaction conditions.[11]

The following procedure for the synthesis of 1-phenyl-*cis*-1-heptene (**8**) is representative (entry 4). To a suspension of cuprous iodide (3.82 g, 20 mmol) in dry THF (50 mL) was added a solution of lithium *cis*-cinnamyl alkoxide (prepared on treatment of *cis*-cinnamyl alcohol (2.68 g, 20 mmol) with ethereal CH_3Li (1.57 M, 12.8 mL) at 0 °C) at room temperature. The mixture was stirred for an additional 30 min before cooling to −78 °C. A hexane solution of *n*-BuLi (39.2 mL, 1.53 M) was added for 10 min, and to the resulting suspension was added a solution of **1** (9.90 g, 20 mmol) in dry DMF (100 mL) for 30 min. The mixture was maintained at the same temperature for 1 h and then warmed to room temperature for 2 h with continuous stirring. After quenching with a saturated NH_4Cl solution (O °C) the ethereal extract was washed with a 0.2 N HCl solution and dried ($MgSO_4$). To the concentrated solution was added light petroleum ether, and precipitated triphenylphosphine oxide was filtered off. Distillation of the filtrate gave a mixture of 1-phenyl-*cis*-heptene (**8**) and 3-phenyl-1-heptene (9) (2.8 g, 80% yield), bp 90-95 °C (4 mmHg). The GLC analysis showed that the relative ratio of **8** and **9** was 96 vs. 4.

The course of the reaction can be readily accounted for, if one assumes that the nucleophilic attack of R^2 of the aminocuprate of the counterion toward the α-carbon of R^1 of **10** in a S_N2 fashion gives R^1-R^2 along with triphenylphosphine oxide and *N*,*N*-methylphenylaminocuprate.

$$\begin{aligned} &R^1OCuR^2_3Li_3 + \mathbf{1} \longrightarrow [R^1OPPh_3{}^+[R^2_3CuN(CH_3)PhLi_2]^- \\ &\qquad\qquad\qquad\qquad \downarrow \qquad\qquad \mathbf{10} \\ &\qquad\qquad R^1R^2 + Ph_3P{=}O + R^2_2CuN(CH_3)PhLi_2 \end{aligned}$$

Work is currently in progress on the extension of this reaction to other systems and application to the synthesis of several natural products.

Acknowledgment. This research was supported in part by Grants from the Ministry of Education, Japan (No. 185192, 110305).

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(2) Prepared as follows: Phenyliminotriphenylphosphorane (mp 128 °C) (L. Horner and H. Oediger, *Justus Liebigs Ann. Chem.*, **627**, 142 (1959)) was reacted with methyl iodide at reflux for 2 h. Removal of excess methyl iodide followed by recrystallization from chloroform–ethyl acetate (1;2) gave **1** quantitatively, mp 238–238.5 °C.

(3) (a) Y. Tanigawa, S.-I. Murahashi, and I. Moritani, *Tetrahedron Lett.*, 471 (1975); (b) Y. Tanigawa, H. Kanamamu, and S.-I. Murahashi, *ibid.*, 4655 (1975).

(4) G. H. Posner, C. E. Whitten, and J. J. Sterling, *J. Am. Chem. Soc.*, **95**, 7788 (1973).

(5) When organolithium compounds are valuable or obtainable only by a several-step synthetic process, addition of 2 molar equiv of triphenylphosphine can substitute for excess organolithium compounds (the relative yield of **3**/**4** = 75/25).

(6) T. L. Mcdonald and W. C. Still, *J. Am. Chem. Soc.*, **97**, 5280 (1975).

(7) E. Dunkelblum, R. Levene, and J. Klein, *Tetrahedron*, **28**, 1009 (1972).

(8) Compound **6**; *m/e* 152; NMR (CCl_4, δ), 2 olefin H at 5.36–5.68 (m), 1 axial, 1 equatorial, and 4 methylene H at 1.22–2.24 (m), 1 axial methyl H at 1.02 (d, J = 3.5 Hz) and 9 methyl H at 0.92 (s), respectively.

(9) When a mixture of 30 vs. 70% of cis and trans alcohols **5** was allowed to react under the same reaction condition, a mixture of cis and trans olefins (**6** and **7**, 70 vs. 30%) was obtained in 68% (bulb-to-bulb distillation, T_{bath} 130 °C (40 mmHg)). Pure **7** was collected by preparative GLC. The spectrum of **7** was as follows (CCl_4, δ); 2 olefin H at 5.24–5.52 (m), 1 axial, 1 equatorial, and 4 methylene H at 1.12–2.32 (m), 1 equatorial methyl H at 0.94 (d, J = 3.5 Hz), and 9 methyl H at 0.92 (s), respectively. Hydrogenation of each of **6** and **7** by utilizing Pd black gave the corresponding cyclohexanes.[10]

(10) C. R. Johnson and G. A. Dutra, *J. Am. Chem. Soc.*, **95**, 7783 (1973).

(11) Simple primary alcohols could be used in the reactions with low conversion under the reaction condition. We have not persuited optimization of the yields, since there are many good alternative methods.[4,10]

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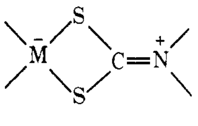
Trimethylgold(III) Complexes of Reactive Sulfoxonium and Sulfonium Ylides

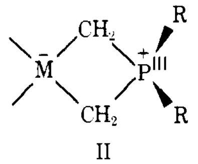
Sir:

Phosphonium ylides have been used for over 20 years[1,2] as reagents for organic synthesis (Wittig reagents). More recently sulfur ylides[3,4] have been found to display important synthetic utility. The pioneering work of Schmidbaur[5] has elucidated the ability of the phosphorus ylides to function as effective organometallic ligands. Recently Kurras et al.[6] and Manzer[7] have extended this work in the transition series of elements.

Our studies[8] and those of others[9,10] have suggested that the ability of dithiocarbamate ligands, I, to delocalize positive charge from the metal center is a determining factor in allowing this ligand to stabilize such unusual oxidation states as Ni^{IV}, Mn^{III}, Cu^{III}, or Fe^{IV}. By analogy we were attracted to Schmidbaur's metal ylide complexes, II, which show remarkable stability for compounds containing transition metal-carbon bonds.[11] Presumably the ability of ylides to remove positive charge from the metal center (reducing the metal) helps to account for their stabilizing influence on metal-carbon bonding. This effect is even more remarkable when one notes that triphenylphosphine does not displace the ylide from $(CH_3)_3AuCH_2P(CH_3)_3$, III



I



II

Sulfur ylides are substantially less stable than phosphorus ylides. However, both $CH_2S(CH_3)_2$ and $CH_2SO(CH_3)_2$ have been generated and utilized[3] in situ. We find that trimethylgold(III) can be used to stabilize these reactive ylides. Furthermore we note that dimethylphenylphosphine can be used