

products in similar experiments with cyclohexene, which they attributed to "insufficient filtering of radiation,"¹⁸ it seems quite likely that the reacting methylene in those experiments also contained a singlet component.¹⁸

(18) See also L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 3665 (1966). Some substrates react with singlet benzophenone before it can cross over to the triplet state.

(19) Applied Research Laboratory, Ford Motor Co., Dearborn, Mich.

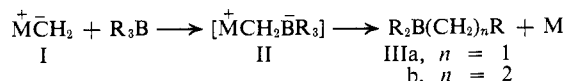
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The Reaction of Functionally Substituted Ylides with Organoboranes

Sir:

We have already reported that dimethyloxosulfonium methylide (I, $M = (CH_3)_2SO$) reacts with organoboranes to afford the corresponding homologated boranes (e.g., IIIa).¹ Since our initial report this reaction has been extended to include several diverse classes of ylides. Thus, both trimethylammonium me-



thylide (I, $M = (CH_3)_3N$)² and triphenylphosphonium methylide (I, $M = (C_6H_5)_3P$)³ have been shown to react with organoboranes in a manner analogous to I. Moreover, we have shown⁴ that use of dimethylsulfonium methylide (I, $M = (CH_3)_2S$) yields principally monohomologated boranes, thus avoiding the problem of higher homologation (i.e., formation of IIIb) apparent in the reactions of the oxosulfonium ylide with boranes. Recently it has been demonstrated⁵ that the homologation of organoboranes can be accomplished through the use of carbon monoxide in the presence of borohydride.

The results of the ylide-organoborane reactions discussed above suggest that boron-bound organic groupings might be functionalized through the selection of an appropriately substituted ylide provided that such ylides would be sufficiently reactive to attack boron and form the requisite betaine intermediates. Such a process, in concert with hydroboration, would provide a facile means of functionalizing olefins.

We wish to report that several functionally substituted ylides do indeed react with organoboranes in a manner analogous to the more reactive methylene ylides. For example, ethyl (dimethylsulfuranylidene)acetate⁶ reacts with a variety of organoboranes (cf. Table I) to afford the corresponding functionally

(1) J. J. Tufariello and L. T. C. Lee, *J. Am. Chem. Soc.*, **88**, 4757 (1966).

(2) W. K. Musker and R. R. Stevens, *Tetrahedron Letters*, 995 (1967).

(3) R. Koster and B. Rickborn, *J. Am. Chem. Soc.*, **89**, 2782 (1967).

(4) J. J. Tufariello, P. Wojtkowski, and L. T. C. Lee, *Chem. Commun.*, 505 (1967).

(5) M. W. Rathke and H. C. Brown, *J. Am. Chem. Soc.*, **89**, 2740 (1967).

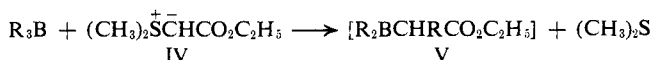
(6) K. W. Ratts and A. N. Yao, *J. Org. Chem.*, **31**, 1185 (1966).

Table I. Functionalization of Olefins by Hydroboration Followed by Reaction with IV

Alkene ^a	Product ^b	Yield, % ^c
1-Hexene	Ethyl <i>n</i> -octanoate	49
1-Heptene	Ethyl <i>n</i> -nonanoate	52
1-Octene	Ethyl <i>n</i> -decanoate	48
2-Methyl-1-pentene	Ethyl 4-methylheptanoate	40
Cyclopentene	Ethyl (cyclopentyl)acetate	35
Norbornene	Ethyl (<i>exo</i> -2-norbornyl)acetate	31
Phenyl ^d	Ethyl phenylacetate	45

^a The hydroboration was carried out so as to ensure the formation of trialkylborane. See ref 7. ^b The products were characterized by direct comparison or by comparison of their physical and chemical properties with those reported in the literature. ^c The yields are based on R_3B using a 4:1 molar ratio of ylide to organoborane. ^d Triphenylborane, purchased from the Aldrich Chemical Co., Milwaukee, Wis.

homologated derivatives. These homologated boranes



are then cleaved to the corresponding saturated esters, rather than the α -hydroxy esters, under the usual conditions of organoborane oxidation⁷ (i.e., alkaline hydrogen peroxide treatment). This latter process is similar to the alkali-induced dealkylation of the monoalkylboranes derived from *cis*- and *trans*- α, α' -dimethylstilbenes and supports the contention that this fission depends on the ability of the boron-bound organic group to sustain a negative charge.⁸ This mode of boron-carbon bond fission may be referred to as hydrolytic cleavage. In the case of V, the cleavage of the functionalized substituent can be brought about by alkali in the absence of peroxide.

When a 1:1 molar ratio of IV to organoborane is used in the reaction, the yields of functionalized ester, obtained after oxidation of the resultant borane, are excellent. Thus 87% of the theoretical amount⁹ of ethyl *n*-nonanoate is obtained from an equimolar mixture of tri-*n*-heptylborane and IV. Similarly 80% of the theoretical quantity of ethyl phenylacetate may be obtained from equimolar amounts of triphenylborane and IV. The efficiency of the process drops markedly after the functionalization of one of the boron-bound groups. The over-all yields of product ester, based on R_3B , are in the range 31-52% if an excess of ylide (i.e., 4:1 molar ratio) is used;¹⁰ however, the unhomologated alcohols, the major by-products in the reaction, are readily separable from the product esters, thus affording the reaction definite synthetic utility. Examination of Table I indicates that less hindered trialkylboranes produce the highest yields of functionalized product.

The general procedure used is illustrated by the reaction between tri-*n*-heptylborane and IV. Tri-*n*-

(7) G. Zweifel and H. C. Brown, *Org. Reactions*, **13**, 1 (1963).

(8) A. J. Weinheimer and W. E. Marisco, *J. Org. Chem.*, **27**, 1926 (1962).

(9) Since the maximum yield of ester to be expected from the reaction of equimolar quantities of organoborane and ylide is 33% based on R_3B , a 29% over-all yield of ester would correspond to 87% of the theoretical amount.

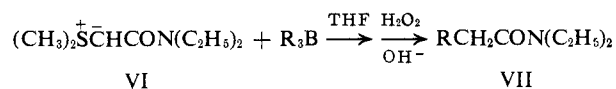
(10) Attempts to functionalize all three boron-bound groups by further increasing the ylide:organoborane ratio were unprofitable, since it was observed that substantial quantities of by-products derived from the ylide were formed in such experiments.

heptylborane (12.1 mmoles), prepared from 1-heptene, 3.92 g (40.0 mmoles), and BH_3 (12.1 mmoles) in tetrahydrofuran,⁷ was added at room temperature to a freshly prepared solution of ethyl (dimethylsulfuranylidene)acetate, prepared⁶ from 12.2 g (53.4 mmoles) of (carbethoxymethyl)dimethylsulfonium bromide, and 1.16 g (48.5 mmoles) of sodium hydride in 200 ml of tetrahydrofuran.

After being stirred for 2 hr at room temperature, the solution was refluxed for an additional 3 hr. The solution was filtered and was treated with 10.0 ml of 3 *N* sodium hydroxide solution and 10.0 ml of 30% hydrogen peroxide at 30–40°. After being stirred for 1 hr at room temperature, the solution was saturated with potassium carbonate and extracted with three 50-ml portions of tetrahydrofuran. At this point, a 52% yield of ethyl *n*-nonanoate was indicated by glpc analysis.

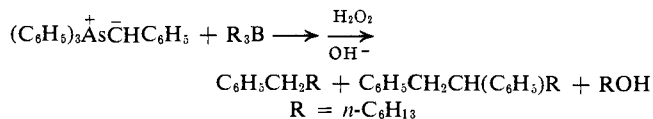
The solvent was removed after the solution was dried over anhydrous magnesium sulfate, and the residue was distilled to afford 2.99 g, 45%, of ethyl *n*-nonanoate, bp 108–109° (8 mm), identified by comparison with an authentic sample.

The reaction of *N,N*-diethyl(dimethylsulfuranylidene)acetamide⁶ (VI) with organoboranes proceeds in a manner analogous to that discussed above. For example, tri-*n*-hexylborane reacts with an equimolar



quantity of VI to afford, after oxidation, 85% of the theoretical yield of the corresponding amide (*i.e.*, VII). Using a 4:1 molar ratio of ylide to organoborane, the over-all yield of VII is *ca.* 50%.

The functionalization of boron-bound groups is not restricted to the use of carbonyl-stabilized ylides such as IV and VI. For example, we have shown that equimolar quantities of triphenylarsonium benzylide¹¹ and tri-*n*-hexylborane react at room temperature under the usual conditions⁴ to afford, after oxidation, 1-phenylheptane and 1,2-diphenyloctane, the product of double homologation, in a 3:1 ratio.¹² Thus, the



product benzylboranes undergo hydrolytic cleavage during the course of the oxidative step.

Acknowledgment. We wish to thank the U. S. Army Research Office (Durham) (DA-ARO-31-124-G889) for generous support of this work.

(11) A. W. Johnson and J. O. Martin, *Chem. Ind.* (London), 1726 (1965).

(12) The corresponding triphenylphosphonium benzylide has been shown³ to react with organoboranes in a similar fashion, albeit under considerably more forcing conditions.

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Additions and Corrections

The Stereochemistry of the Coordination Group in an Iron(III) Derivative of Tetraphenylporphine [*J. Am. Chem. Soc.*, **89**, 1992 (1967)]. By J. L. HOARD, G. H. COHEN, AND M. D. GLICK. Department of Chemistry, Cornell University, Ithaca, New York 14850.

On page 1994 in Table I, the entries under B_x and B_y (columns 5 and 6) for Cl (line 2) should both read 5.4.

One-Step Synthesis of Bridged Aziridines [*J. Am. Chem. Soc.*, **89**, 5045 (1967)]. By WATARU NAGATA, SHOICHI HIRAI, KYOZO KAWATA, AND TSUTOMU AOKI. Shionogi Research Laboratory, Shionogi & Co., Ltd., Fukushima-ku, Osaka, Japan.

On page 5045, column 2, in line 11, $\text{C}_{22}\text{H}_{35}\text{O}_3\text{N}$ should read $\text{C}_{22}\text{H}_{33}\text{O}_3\text{N}$; in line 16, $\text{C}_{20}\text{H}_{29}\text{O}_3\text{N}$ should read $\text{C}_{20}\text{H}_{27}\text{O}_3\text{N}$; in line 19, $\text{C}_{20}\text{H}_{29}\text{O}_3\text{N}$ should read $\text{C}_{20}\text{H}_{27}\text{O}_3\text{N}$; and in line 24, $\text{C}_{22}\text{H}_{34}\text{O}_3\text{NI} \cdot 0.5\text{H}_2\text{O}$ should read $\text{C}_{22}\text{H}_{32}\text{O}_3\text{NI} \cdot 0.5\text{H}_2\text{O}$.

A New Method for Isoquinuclidine Synthesis. A Total Synthesis of Desethylbogamine [*J. Am. Chem. Soc.*, **89**, 5046 (1967)]. By WATARU NAGATA, SHOICHI HIRAI, KYOZO KAWATA, AND TAMOTSU OKUMURA. Shionogi Research Laboratory, Shionogi & Co., Ltd., Fukushima-ku, Osaka, Japan.

On page 5047, column 2, in line 9, $\text{C}_{17}\text{H}_{22}\text{N}_2\text{O}_2$ should read $\text{C}_{17}\text{H}_{20}\text{N}_2\text{O}_2$.

Stereoselectivity in Hydrogen Atom Transfer to the Vinyl Radicals Derived from the *cis*- and *trans*-*t*-Butyl α -Chloropercinnamates [*J. Am. Chem. Soc.*, **89**, 5251 (1967)]. By LAWRENCE A. SINGER AND NOLAN P. KONG. Department of Chemistry, University of Chicago, Chicago, Illinois 60639.

In footnote 15, we incorrectly cited the olefin distribution obtained from the thermal decomposition of either *cis*- or *trans*-*t*-butyl α -methylpercinamate in cumene as *trans*:*cis* = 60:40. It should read *trans*:*cis* = 40:60 [L. A. Singer and N. P. Kong, *J. Am. Chem. Soc.*, **88**, 5213 (1966)]. This error invalidates the argument (on page 5254) which claims that the similarity of this ratio to that obtained from the *cis*- α -chloro system is a means of deciding that the product ratios obtained from the *cis*- α -chloro perester were more nearly the expected ones whereas those from the *trans*- α -chloro perester were richer in *cis* olefin than expected. This argument presumes that the stereoselectivity features of the α -chloro- β -phenylvinyl radical and the α -methyl- β -phenylvinyl radical are the same. In retrospect, the stereoselectivity features of the hydro-