A pK value of 11.14 for malononitrile in aqueous solution was determined by Bowden and Stewart.[5] This acid was then used as the "anchor compound" to establish an acidity scale in ethanol–dimethyl sulfoxide mixtures. The scale was applied to the measurement of pK values for a number of carbon acids, among which were 9-carbomethoxyfluorene, tris(*p*-nitrophenyl)methane, and 9-phenylfluorene. The pK(H_2O) values shown in the table for these compounds are those obtained by Bowden and Stewart.

The present data clearly show the breakdown of the acidity scale. The relative acidity of malononitrile and 9-carbomethoxyfluorene changes by 2.5 pK units on going from ethanol to dimethyl sulfoxide solution. The relative acidities of 9-carbomethoxyfluorene and either tris(*p*-nitrophenyl)methane or 9-phenylfluorene, however, are nearly the same in both determinations.

In now appears probable that the agreement previously reported[2] between our "absolute" pK's and those determined by Steiner[6] by acidity function techniques is purely fortuitous. Apparently, the reference compound, 4-nitroaniline, used by Steiner for determination of the other acids just happens to be one for which the pK is not strongly affected by the change of solvent. Malononitrile appears to be another such compound, showing the same pK in water and dimethyl sulfoxide.

As we discussed in our previous paper,[2] four distinct effects are expected to influence the change in acidity of an acid on going from water to dimethyl sulfoxide. Two of these effects, the greater basicity of dimethyl sulfoxide than water and the dispersion interaction of highly colored anions with solvent, would act to increase acidity in dimethyl sulfoxide. The other two effects, electrostatic effects and hydrogen bonding of solvent to the conjugate base, would decrease acidity in dimethyl sulfoxide. For the nitroanilines and for malononitrile it appears that these effects just balance. We believe that this cancellation is purely fortuitous and even results from different magnitudes of the individual effects in the two cases. Both hydrogen bonding and the dispersion interactions are expected to be greater for the nitroanilines than for malononitrile.

The increase in acidity of 9-carbomethoxyfluorene over that for malononitrile in going from ethanol to dimethyl sulfoxide is most reasonably attributed to the dispersion interactions of the substituted fluorenyl anion with the polarizable solvent.

Two conclusions pertinent to current investigations in the study of acidities of hydrocarbons can be drawn from our present data. First, and in our opinion most important, *the data clearly show that no single H-acidity function applicable to acids of different structures can be constructed to reach into pure dimethyl sulfoxide.* This conclusion is further strengthened by the results of Steiner's recent study.[7]

Second, if the relative acidities of various hydrocarbons in cyclohexylamine solution, determined by Streitwieser,[4] are adjusted to our value of 16.4 for the pK of 9-phenylfluorene, rather than to the previously used value of 18.5, the discrepancies noted between the scales in dimethyl sulfoxide and cyclohexylamine solutions no longer appear, and, in fact, the agreement, as shown in Table I, is even better than might have been expected for two such different solvents.

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Received February 23, 1967

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A Novel Method for the Synthesis of Isomerically Pure Vinyl Halides from Alkynes *via* the Hydroalumination Reaction[1]

Sir:

The addition of bromine to vinylorganoboranes results in the formation of 1,2-dibromoboranes. These derivatives are converted to vinyl halides when treated with water or aqueous sodium hydroxide.[2] Recently, Matteson and Liedtke[3] have suggested that bromine adds *trans* to unsaturated boronic esters, and they have established that deboronobromination involves a stereospecific *trans* elimination. In concurrence with these results is the observation by Brown[2] that bromination of *trans*-1-hex-1-enyl-bis(3-methyl-2-butyl)borane, derived from hydroboration of 1-hexyne with bis(3-methyl-2-butyl)borane,[4] gives after hydrolysis *cis*-1-bromo-1-hexene.

We have now investigated the halogenation of vinylalanes. These derivatives are readily available by hydroalumination of alkynes with diisobutylaluminum hydride in a hydrocarbon solvent.[5] This involves a *cis* addition of the aluminum–hydrogen bond to the triple bond, yielding *trans*-vinylalanes from 1-alkynes and *cis*-vinylalanes from disubstituted alkynes. Treatment of the *trans*-vinylalane derived from 1-hexyne in tetrahydrofuran with various halogens in a 1:1 ratio at −50° produces essentially pure *trans*-1-halo-1-hexenes. Under similar experimental conditions the *cis*-vinylalane obtained from 3-hexyne reacts with bromine or iodine to give the corresponding *cis*-3-halo-3-hexenes. The experimental results are summarized in Table I.

The fact that halogenation of unsaturated alanes proceeds with retention of configuration supports the contention that vinylalanes undergo electrophilic cleavage (1) preferentially at the vinyl carbon–aluminum bond. Formation of vinyl halides from vinylboranes, however, is the result of an addition–elimination reaction (2). It should be noted that the reaction of chlorine with the vinylalane derived from 1-hexyne gives a 70:30 mixture of *trans*- and *cis*-1-chloro-1-hexene, indicating a competition between addition to the double bond and cleavage at the vinyl carbon–aluminum bond.

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(1) This research was supported by National Science Foundation Grants No. GP3521 and GP 6633.

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(3) D. S. Matteson and J. D. Liedtke, *J. Am. Chem. Soc.*, **87**, 1526 (1965).

(4) H. C. Brown, and G. Zweifel, *ibid.*, **83**, 3834 (1961).

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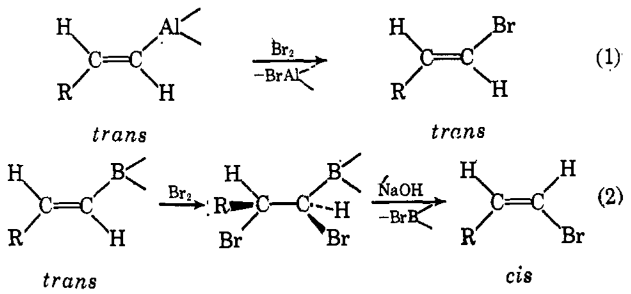
Table I. Halogenation of Vinylalanes in Tetrahydrofuran

Vinylalane derived from	Halogen[a]	Vinyl halide, *trans*	%[b,c] *cis*
1-Hexyne	I_2	94	<2
	ICl	76[d]	<2
	Br_2	72	<2
3-Hexyne	I_2	<2	72
	Br_2	<2	42

[a] Both bromine and iodine monochloride were dissolved in methylene chloride and then added to the vinylalane. Iodine was used in tetrahydrofuran. [b] Analysis by glpc with an internal standard. [c] The assignments for the vinyl halides are based on infrared and nmr data. [d] *trans*-1-Iodo-1-hexene.

With increasing reactivity of the halogen, there is less discrimination between cleavages at the hexenyl–aluminum and isobutyl–aluminum bonds. In these cases the vinyl halide is contaminated with the isobutyl halide. In order to maximize the yield of the vinyl halide, larger amounts of halogens should be used.



The simplicity of this procedure makes it a valuable method for synthesis of isomerically pure vinyl halides. The isobutyl groups on aluminum do not interfere with the isolation of the halides since they are converted to isobutane in the hydrolysis step. It is of special importance in that 1-iodo-1-alkenes, which cannot be prepared by the addition of hydrogen iodide to 1-alkynes in the presence of peroxides, are obtained in excellent yield from the corresponding vinylalanes. A representative procedure is given below.

To 0.10 mole of 1-hexyne in 20 ml of *n*-heptane was added 0.10 mole of diisobutylaluminum hydride while maintaining the temperature below 40°. When the initial exothermic reaction had subsided, the reaction mixture was heated for 2 hr at 50°. The heptane was then removed under reduced pressure (0.5 mm), and the residue obtained was diluted with 40 ml of tetrahydrofuran. To this vinylalane solution at $-50°$ was added 0.10 mole of iodine in 40 ml of tetrahydrofuran. After allowing the reaction mixture to warm up to room temperature, the diisobutylalane ($-Al(C_4H_9)_2$) was decomposed at 20–30° by dropwise addition of 20% sulfuric acid (exothermic reaction). When the isobutane evolution had diminished, the reaction mixture was poured into ice–20% H_2SO_4. The vinyl iodide was extracted into pentane and the combined extracts were washed first with sodium thiosulfate, then with sodium bicarbonate. Distillation gave 15.52 g of *trans*-1-iodo-1-hexene (74%); bp 50–52° (3 mm), $n^{23}\text{D}$ 1.5072. A small amount of the vinyl iodide was converted to the vinyllithium derivative,[6] which was hydrolyzed with deuterium oxide. The infrared and nmr spectra of the olefin obtained were identical with those of an authentic sample of *trans*-1-hexene-1-d_1.

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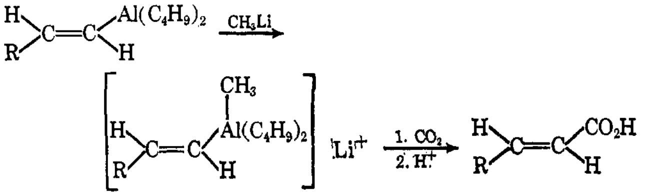
A New and Convenient Method for the Preparation of Isomerically Pure α,β-Unsaturated Derivatives *via* Hydroalumination of Alkynes

Sir:

Relatively little attention has been directed to the utilization of organoalanes as Grignard-like reagents. Ziegler and co-workers[1] have shown that the addition of carbon dioxide to trialkylalanes at atmospheric pressure and at room temperature in hydrocarbon solvents results in the carbonation of only one carbon–aluminum bond. Similarly, we have observed that carbonation of vinylalanes in hydrocarbon solvents affords the corresponding α,β-unsaturated acids in modest yields (30–37%). Both trialkylalanes and vinylalanes, however, fail to react with carbon dioxide in ether or hydrocarbon–ether mixtures at room temperature.

We now wish to report that the *ate* complexes of vinylalanes may be utilized for Grignard-type reactions. The required vinylalanes are readily accessible *via* hydroalumination of alkynes with diisobutylaluminum hydride in hydrocarbon solvents.[2,3] This involves a *cis* addition of the aluminum–hydrogen bond to the triple bond, yielding *trans*-vinylalanes from 1-alkynes and *cis*-vinylalanes from disubstituted alkynes. Treatment of the hydrocarbon solutions of vinylalanes with methyllithium in ether in a 1:1 ratio followed by carbonation gives the corresponding carboxylic acids in excellent yields. Likewise, acetaldehyde and paraformaldehyde[4] may be treated with the *ate* complexes at 25 and 35°, respectively, to yield α,β-unsaturated alcohols. A summary of the experimental results of these reactions is given in Table I.



Examination of the reaction mixtures by glpc revealed that the products obtained in each case were isomerically pure. Consequently, the reactions of vinylalanates with Grignard co-reagents proceed with retention of configuration. It was also noted that carbonation occurs exclusively at the vinyl–aluminum bond. The isobutyl moieties of the hydroaluminating agent are converted to isobutane in the hydrolysis step, and hence do not interfere in the isolation of the products.

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(2) G. Wilke and H. Müller, *ibid.*, **629**, 222 (1960).

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(4) It has been reported that the reaction of Grignard compounds with paraformaldehyde proceeds very slowly, whereas organolithium derivatives react at a much faster rate: A. Schaap, L. Brandsma, and J. F. Arens, *Rec. Trav. Chim.*, **84**, 1200 (1965).