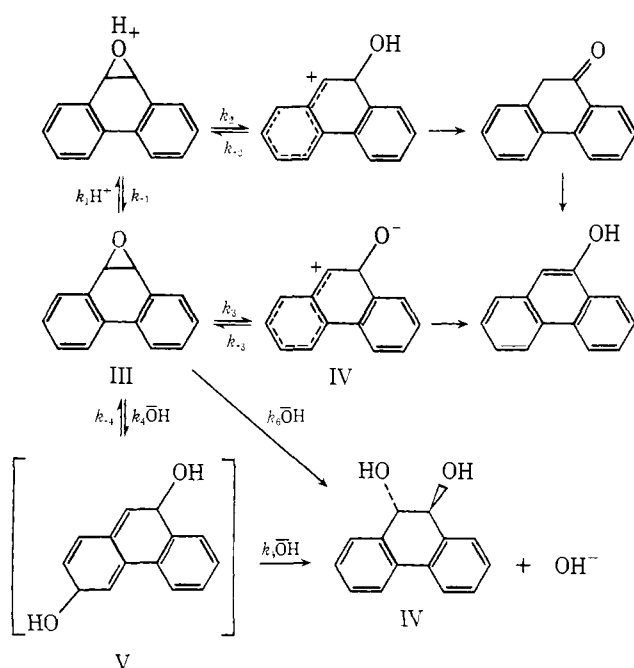


Figure 1. pH-rate profile for the rearrangement of 9,10-phenanthrene oxide (H_2O , $\mu = 1.0$, 30°). Arrows point to duplicate determinations for 9,10-dideuterio-9,10-phenanthrene oxide. Insert to figure: pH-rate profiles for the rearrangement of 3,4-phenanthrene oxide (\blacksquare), 1,2-phenanthrene oxide (\blacktriangle), and 9,10-phenanthrene oxide (\bullet). (50% dioxane-water, $\mu = 0.1$, 30°).

Scheme I



$$\begin{aligned}
 k_2 K_1 &= 1.0 \times 10^2 M^{-1} \text{sec}^{-1} \\
 k_3 &= 2.1 \times 10^{-1} \text{sec}^{-1} \\
 k_4/k_{-4} &= 4.26 \times 10^6 \\
 k_5 &= 4.73 \times 10^{-4} M^{-1} \text{sec}^{-1} \\
 k_6 &= 1.07 \times 10^2 M^{-1} \text{sec}^{-1} \\
 K_{IV} &= 1.48 \times 10^{-14}
 \end{aligned}$$

example, benzene oxides and 1,2-naphthalene oxide do not react with HO^- .^{5-7,9} Phenols are their products of rearrangement regardless of pH; the corresponding *trans*-dihydrodiols are obtained only *via* enzymatic hydration.¹⁰ In addition III, unlike the non-K-region arene oxides,¹¹ has been found to react rapidly with primary and secondary amines. Mercaptide ions have

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(11) A. M. Jeffrey, H. J. C. Yeh, D. M. Jerina, R. M. DeMarinis, C. H. Foster, D. E. Piccolo, and G. A. Berchtold, *J. Amer. Chem. Soc.*, in press.

been shown to provide enhanced rates of disappearance of benzene oxide from aqueous solution (Brønsted $\beta = 0.2$),¹² but their reaction with III is even more marked. The stereochemistry for the addition of nucleophiles to arene oxides is generally *trans*.¹¹ The question of nucleophilic attack on III *vs.* IV and a detailed account of the reaction of III with amines, mercaptide ions, proteins, and nucleic acids will be presented in the full paper.

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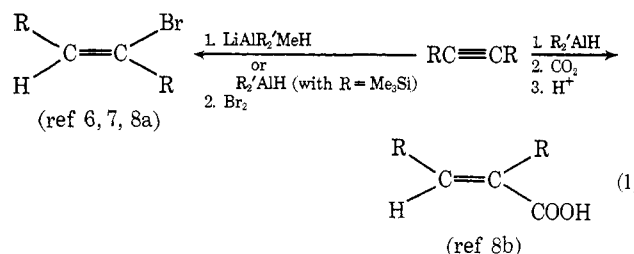
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Stereospecific Hydralumination of Alkenes and the Stereochemistry of Reactions at Alkyl Carbon-Aluminum Bonds¹

Sir:

The stereospecific *cis*²⁻⁵ or *trans*^{4,6} hydralumination of alkynes, coupled with substitution and insertion reactions on the resulting vinylic aluminum adducts that occur with retention of configuration, is an important synthetic route to stereoregulated alkenes and their derivatives⁶⁻⁹ (eq 1).



Extension of such stereospecific hydraluminations and subsequent derivatizations to alkenes has been beset, up to the present, with two difficulties: (a) hydraluminations of alkenes, especially of the vicinally disubstituted ethylenic type, proceed at much slower rates;¹⁰ and (b) more discouragingly, nmr studies have shown that, in

(1) Part XXIX of the series, "Organometallic Compounds of Group III," devoted to carbometalation and hydrometalation, cf. J. J. Eisch and S.-G. Rhee, *J. Organometal. Chem.*, in press, for the previous part.

(2) G. Wilke and H. Müller, *Justus Liebigs Ann. Chem.*, **629**, 222 (1960).

(3) J. J. Eisch and W. C. Kaska, *J. Amer. Chem. Soc.*, **88**, 2213 (1966).

(4) J. J. Eisch and M. W. Foxton, *J. Organometal. Chem.*, **11**, P50 (1968); *J. Org. Chem.*, **36**, 3520 (1971).

(5) J. J. Eisch and R. Amtmann, *J. Org. Chem.*, **37**, 3410 (1972).

(6) G. Zweifel and R. B. Steele, *J. Amer. Chem. Soc.*, **89**, 5085 (1967).

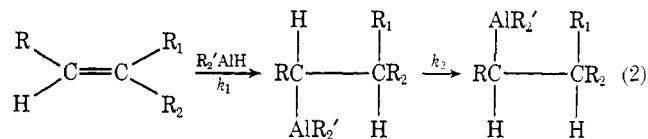
(7) G. Zweifel and C. C. Whitney, *J. Amer. Chem. Soc.*, **89**, 2753 (1967).

(8) (a) J. J. Eisch and G. Gupta, unpublished work; (b) J. J. Eisch and M. W. Foxton, *J. Organometal. Chem.*, **11**, P7 (1968).

(9) Cf. H. Lehmkuhl, K. Ziegler, and H.-G. Gellert in "Houben-Weyl Methoden der Organischen Chemie," Vol. XIII/4, E. Müller, Ed., Georg Thieme Verlag, Stuttgart, 1970, pp 204-258.

(10) (a) K. Ziegler, H.-G. Gellert, H. Martin, K. Nagel, and J. Schneider, *Justus Liebigs Ann. Chem.*, **589**, 91 (1954); (b) G. Hata, *Chem. Commun.*, 7 (1968).

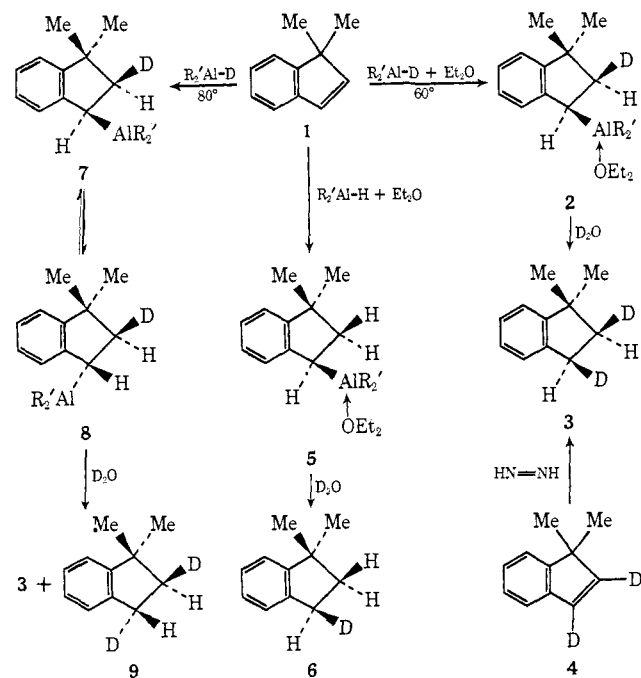
hydrocarbon solvents, the alkyl carbon–aluminum bond undergoes inversion at moderate temperatures.¹¹ The combination of these two factors could destroy any initial stereochemical bias in the hydralumination ($k_2 \geq k_1$, eq 2). However, although diethyl ether has



been reported to slow down the inversion process,¹² such a donor solvent also retards the hydralumination.⁴

We wish to report now our success in finding a suitable olefinic substrate and experimental conditions that circumvent these difficulties and permit us to define the stereochemistry of hydralumination. By choice of the strained olefin, 1,1-dimethylindene (**1**), for which k_1 is enhanced (cf. ref 10a), and by hydraluminating with diisobutylaluminum deuteride in the presence of diethyl ether, we have found that treatment of the adduct (**2**) with D_2O yields pure *cis*-2,3-dideuterio-1,1-dimethylindan (**3**), which was identical in its infrared spectrum¹³ with an authentic sample prepared by the diimide reduction of 2,3-dideuterio-1,1-dimethylindene¹⁴ (**4**). These findings demonstrate that the addition of $\text{R}_2'\text{Al-D}$ occurs stereospecifically *cis* to **1** and that the configuration is stable in the presence of ether. Furthermore, treatment of **1** with $\text{R}_2'\text{Al-H}$ and subsequent treatment with D_2O yielded only 3-deuterio-1,1-dimethylindan (**6**), demonstrating that the aluminum precursor **5** was formed regiospecifically as well (Scheme I).

Scheme I

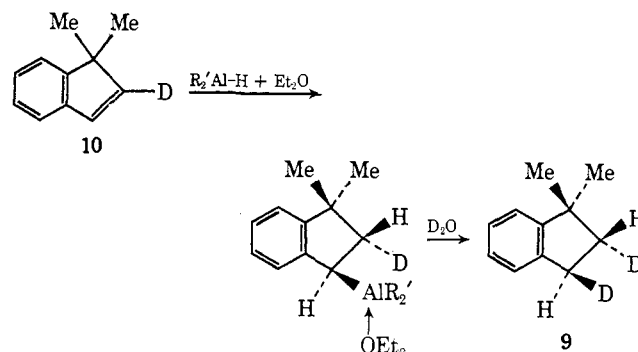


(11) G. Fraenkel, D. T. Dix, and M. Carlson, *Tetrahedron Lett.*, 579 (1968).

(12) M. Witanowski and J. D. Roberts, *J. Amer. Chem. Soc.*, **88**, 737 (1966).

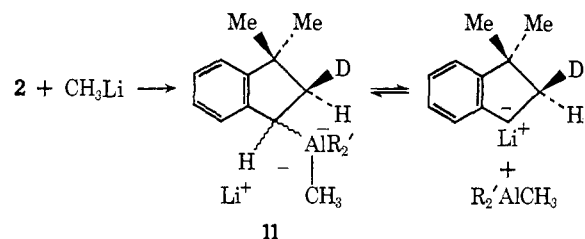
(13) The *cis*-2,3-dideuterio-1,1-dimethylindan possesses an infrared band (neat) at $724(\text{s})\text{ cm}^{-1}$, which distinguishes it cleanly from the *trans* isomer, which has bands (neat) at $736(\text{m})$ and $729(\text{s})\text{ cm}^{-1}$. The dideuterated character was verified by the falling drop method (*cis*,

As a measure of the efficacy of the ether in maintaining the configuration of **2**, it was shown that the addition of $\text{R}_2'\text{Al-D}$ to **1** in the absence of ether, followed by treatment with D_2O , led to a 1:1 mixture of the *cis*- and *trans*-2,3-dideuterio-1,1-dimethylindans (**3** and **9**). An authentic sample of **9** was procured by treating 2-deuterio-1,1-dimethylindene (**10**) with $\text{R}_2'\text{Al-H}$ in the



presence of diethyl ether and then hydrolyzing with D_2O .

Having an alkyl carbon–aluminum bond in structure **2** of defined stereochemistry, we were now able to observe the stereochemical course of cleavage reactions. Although it is clear from Scheme I that simple hydrolysis of **2** occurs with retention of configuration at C_3 , other donors respond differently. The addition of pyridine to **2** before addition of D_2O still yields pure **3**, but the introduction of between 0.2 and 1.5 equiv of methyl lithium prior to the D_2O results eventually in a 1:1 mixture of **3** and **9**. Clearly, the aluminate complex (**11**) must undergo reversible dissociation into a benzylic-like carbanion that inverts the C_3 configuration.

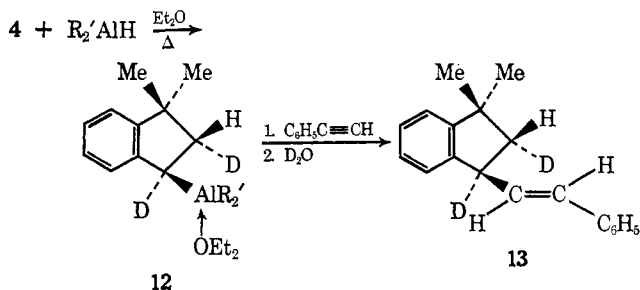


Finally, the interaction of such etherates in an insertion reaction with phenylacetylene was shown to occur with retention of configuration. Heating an ether solution of **12** with phenylacetylene up to 110° for several days gave, as the principal product, **13**,¹⁵ *cis*-2,3-dideuterio-1,1-dimethyl-3-(*trans*- β -styryl)indan, which had the following spectral characteristics: infrared (neat), $2185(\text{w})$, $967(\text{s})$, (*trans*- $\text{CH}=\text{CH}-$), 766

96.9% d_2 ; *trans*, 100% d_2 ; cf. A. S. Keston, D. Rittenberg, and R. Schoenheimer, *J. Biol. Chem.*, **122**, 227 (1938). It might be recalled that the *meso*- and *l*-2,3-dideuteriobutanes also possess different infrared spectra: G. K. Helmkamp and B. F. Rickborn, *J. Org. Chem.*, **22**, 479 (1957).

(14) Compound **1** was prepared *via* 3,3-dimethyl-1-indanone obtained from neophyl chloride (L. Ames, E. Chaitman, and F. Grant, *J. Org. Chem.*, **26**, 1299 (1961)). Reduction of the ketone with LiAlH_4 , followed by acid-catalyzed dehydration of the resulting alcohol, gave **1**. Base-catalyzed deuterium exchange on the ketone, followed by treatment with LiAlH_4 or LiAlD_4 and then dehydration of the alcohol, gave **10** or **4**, respectively.

(15) The unreacted **12** was accounted for, and identified by infrared spectroscopy, as 1,1-dimethylindan-2,3,3-*ds*. The absence of *cis*-2,3-dideuterio-1,1-dimethylindan (**3**) proved that phenylacetylene did not cleave **12** in a protodemetalation side-reaction. A minor product (ca. 30% of **13**), isomerizable into **13** on the glc silicone gum rubber column used in collecting **13** (250°), seems to be the 3-(*cis*- β -styryl)indan.



(s), 752 (s), 736 (s), and 695 (s) cm^{-1} ; nmr (CDCl_3 , H_2 decoupled), δ 1.21 (s, CH_3), 1.39 (s, CH_3), 1.81 (s, $\text{C}_2\text{-H}$), 6.16 (d, $J = 15.5$ Hz), 6.54 (d, $J = 15.5$ Hz), and 6.9–7.5 (m, 9 H). The syn character of the $\text{C}_2\text{-H}$ with respect to the β -styryl group in **13** is founded upon an nmr analysis of an authentic sample of 1,1-dimethyl-3-vinyllindan¹⁶ (**14**), whose spectrum in CDCl_3 at 100 MHz gave a well-defined ABX pattern for the C_2 and C_3 protons (δ): 1.68 (broadened d of d, H_2 cis to vinyl, $J_{\text{gem}} = 12.6$ Hz and $J_{\text{trans}} = 9.3$ Hz), 2.13 (sharp d of d, H_2 trans to vinyl, $J_{\text{cis}} = 7.6$ Hz), and 3.77 (broadened d of d, H_3). The literature on such nmr spectral data leads to the conclusion that protons cis to a vinylic group lie within the π -electron shielding cone and hence absorb at higher fields than the trans protons (cf. δ 1.81 ppm for **13** and 1.68 for **14**).¹⁷ Furthermore,

(16) The authors are indebted to Dr. K. E. Möller of the Max-Planck-Institut für Kohlenforschung, Mülheim (Ruhr), Federal Republic of Germany, for a sample of 1,1-dimethyl-3-vinyllindan (K. E. Möller, *Brennst.-Chem.*, **44**, 175 (1963)).

(17) (a) F. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969, pp 72–75; (b) G. Schumpf, *Tetrahedron Lett.*, 2571 (1970); (c) D. Merkel and G. Köbrich, *Chem. Ber.*, **106**, 2025 (1973); (d) B. M. Jacobson and P. D. Bartlett, *J. Org. Chem.*, **38**, 1030 (1973).

as in vinylcyclopropane,^{17b} the long-range coupling between the vinyl hydrogens and the vicinal cis hydrogen should be larger than that with the trans hydrogen. The assignment of structure **13** to the product does then account for the broadened resonances centered at 1.68 ppm for **14**.

Thus, we have demonstrated that hydralumination of a model alkene can be directed to occur in a stereospecifically cis fashion and that synthetically useful cleavage and insertion reactions can be achieved with either complete or highly favored retention of configuration. Although synthetic applications are encumbered by the retarding effect of ethers and amines on the rate of hydraluminating alkenes, we have also observed that addition of 1–2% of nickel salts,¹⁸ with or without phosphines, can catalyze the hydralumination of **1** without loss of cis stereospecificity. Furthermore, the presence of triphenylphosphine can alter the regioselectivity of the nickel-catalyzed hydralumination from an 80:20 mixture of 3-alumino- and 2-alumino-1,1-dimethylindans to solely the 3-alumino isomer (cf. **5**).

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