The Reaction of 1-Alkynes with Organometallic Compounds. II. The Relationship between Decomposition Potentials of Grignard Reagents and Their Relative Reactivity Toward Terminal Acetylenes

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An investigation of reaction 1 has revealed that the

$$\underset{1\,M}{R\text{—}C{\equiv}CH} + \underset{1\,M}{R'MgX} \xrightarrow{Et_2O} R'H + R\text{—}C{\equiv}C\text{—}MgX \qquad (1)$$

rate of evolution of the hydrocarbon R′H is dependent upon the nature of R, R′ and X. The effects of varying R′ and X,[2a] and R,[2b] have been reported previously. Relative reactivities have been assigned by comparison of the half-lives, $t_{1/2}$, of reaction 1.

Attention has been called[2a] to the apparent role of the number of β-hydrogens of R′MgX with reference to relative reactivity. A very interesting correlation of the data now can be made with the decomposition potentials, E_d, of Grignard reagents as determined by Evans, *et al.*[3] Table I lists all of the Grignard reagents for which both values are available.

Table I

Grignard reagent	Rel. reactivity[a]	Decompn. voltage, E_d[a]
MeMgBr	6	1.94
n-PrMgBr	59	1.42
EtMgBr	100	1.28
i-PrMgBr	210	1.07
AllylMgBr	435	0.86

[a] 1 molar concentrations.

A plot of E_d against the logarithm of the relative reactivity is shown in Fig. 1 and is linear. This would indicate that there is a linear relationship between a free energy quantity associated with the electrolysis of Grignard reagents and a free energy in the reactions of such Grignard reagents with the acidic hydrogen in terminal acetylenes. However, since a Grignard reagent is a complex mixture and the mechanism of discharge reactions is also complex, one cannot arrive at this time at a satisfactory explanation for the observed correlation.

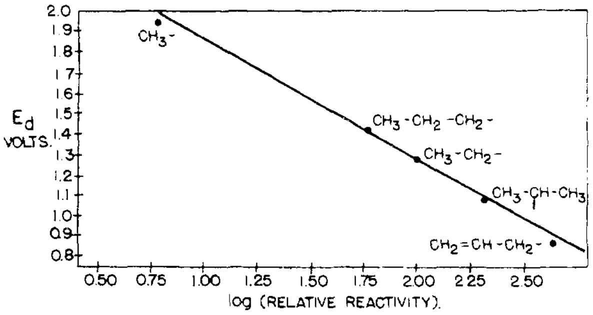

Fig. 1.—Plot of decomposition voltage of RMgBr against log (relative reactivity), as determined by the reaction RMgBr + $C_4H_9C{\equiv}CH \rightarrow RH + C_4H_9C{\equiv}CMgBr$.

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[2] (a) J. H. Wotiz, C. A. Hollingsworth and Raymond E. Dessy, This Journal, **77**, 103 (1955); (b) J. H. Wotiz, C. A. Hollingsworth and Raymond E. Dessy, Abstracts, 128th Meeting of the American Chemical Society, Cincinnati, Ohio, 1955.

[3] W. V. Evans, F. H. Lee and C. H. Lee, This Journal, **57**, 489 (1935).

The Preparation of *cis*-2-Chlorostilbene and its Reaction with Lithium

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In the preparation of *cis*-2-stilbenecarboxylic acid, *cis*-2-chlorostilbene or *cis*-2-bromostilbene are potentially useful intermediates for either the carbonation of an organometallic compound or for the Rosenmund–von Braun nitrile synthesis. The availability of *o*-chlorobenzaldehyde prompted a preliminary investigation of the use of the chlorine series. The condensation of the aldehyde with phenylacetic acid and the decarboxylation of the *trans*-α-phenyl-2-chlorocinnamic acid went as planned,[3] but the conversion of the *cis*-2-chlorostilbene to the lithium derivative seemed to go in only fair yield, and the acid obtained was the *trans*-2-stilbenecarboxylic acid rather than the *cis*-acid.

Experimental[4]

***trans*-α-Phenyl-2-chlorocinnamic Acid.**—A mixture of 500 ml. of acetic anhydride, 70.5 g. (55 ml., 0.5 mole) of *o*-chlorobenzaldehyde, 100 g. (0.75 mole) of phenylacetic acid and 50 g. (68.75 ml., 0.5 mole) of triethylamine was heated at reflux temperature for 1.5 hours, cooled to about 80° and then 250 ml. of water added slowly with swirling. The mixture was brought to boiling and filtered. On cooling, 85 g. of *trans*-α-phenyl-2-chlorocinnamic acid crystallized as needles; the crude acid suitable for decarboxylation varied from colorless to light yellow, m.p. 175.5–176.5°. From the mother liquor 12 g. of an acid mixture, m.p. 140–152°, could be obtained. An analytical sample was prepared by decolorizing a solution of the crude product in 10% NaOH, and by recrystallizing the recovered acid from 75% acetic acid, m.p. 176–176.5°.

Anal. Calcd. for $C_{15}H_{11}O_2Cl$: C, 69.64; H, 4.28. Found: C, 69.67; H, 4.21.

***cis*-2-Chlorostilbene.**—One hundred milliliters of redistilled quinoline and 3 g. of copper chromite catalyst were heated to 230° in a round-bottomed three-necked flask, fitted with a stirrer, a thermometer and a funnel for addition of a solid. Thirty grams of *trans*-α-phenyl-2-chlorocinnamic acid was added at such a rate that the temperature did not drop below 225°. When the vigorous evolution of CO_2 had stopped (about 20 min.) the catalyst was removed by filtration and the filtrate was poured into a solution of 200 ml. of concd. hydrochloric acid diluted to 600 ml. The mixture was extracted thoroughly with methylene chloride, and the methylene chloride layer was washed with 10% HCl, 10% NaOH and finally with water several times. After drying, the solvent was removed, leaving the crude *cis*-2-chlorostilbene as a dark brown oil. Five such runs were combined and distilled twice under reduced pressure in a nitrogen atmosphere to give a yellow oil, b.p. 118–120° at 1.5–2 mm.; yield 100 g., 80%. The infrared curve showed that less than 1% of the *trans* isomer was present.

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[3] D. F. DeTar and Y. W. Chu, This Journal, **76**, 1686 (1954); *cf.* P. Ruggli and A. Staub, *Helv. Chim. Acta*, **20**, 37 (1937).

[4] All melting points are corrected.