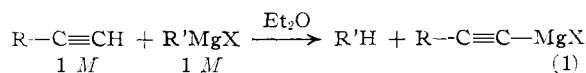


The Reaction of 1-Alkynes with Organometallic Compounds. II. The Relationship between Decomposition Potentials of Grignard Reagents and Their Relative Reactivity Toward Terminal Acetylenes

BY RAYMOND E. DESSY,¹ C. A. HOLLINGSWORTH AND JOHN H. WOTIZ

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An investigation of reaction 1 has revealed that the



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
<i>n</i> -PrMgBr	59	1.42
EtMgBr	100	1.28
<i>i</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,

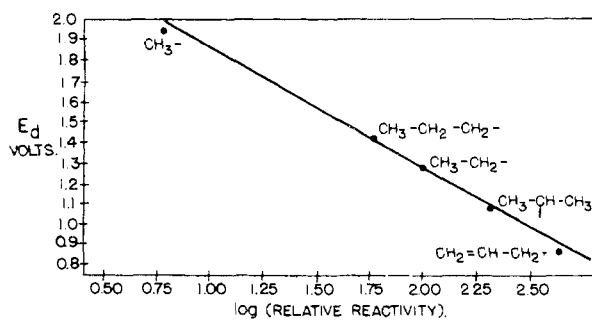


Fig. 1.—Plot of decomposition voltage of RMgBr against log (relative reactivity), as determined by the reaction $\text{RMgBr} + \text{C}_4\text{H}_9\text{C}\equiv\text{CH} \rightarrow \text{RH} + \text{C}_4\text{H}_9\text{C}\equiv\text{CMgBr}$.

(1) National Science Foundation Predoctoral Fellow.

(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).

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.

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

BY DELOS F. DETAR¹ AND YUN-WEN CHU²

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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 Braum 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.

Experimental⁴

***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 $\text{C}_{15}\text{H}_{11}\text{O}_2\text{Cl}$: 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.

Anal. Calcd. for $C_{14}H_{11}Cl$: C, 78.31; H, 5.16. Found: C, 78.50; H, 5.14.

trans-2-Chlorostilbene.—One gram of *cis*-*o*-chlorostilbene was isomerized with 10 ml. of nitrobenzene and a few crystals of iodine at reflux temperature for twenty minutes. The solvent was removed and the *trans*-2-chlorostilbene was distilled, b.p. 138–140° at 2 mm. The oil solidified and was recrystallized from methanol giving colorless prisms, m.p. 39–40°; reported⁵ m.p. 40°.

Attempted Synthesis of *cis*-Stilbene-2-carboxylic Acid.
(1).—In a dry nitrogen-flushed 200-ml. three-necked round-bottomed flask provided with a stirrer, dropping funnel and a reflux condenser, the latter two protected with calcium chloride drying tubes was placed 1 g. (0.14 mole) of lithium metal ribbon cut into small pieces. A solution of 20 g. (0.097 mole) of *cis*-2-chlorostilbene in 50 ml. of anhydrous ether was then added dropwise at room temperature with vigorous stirring over a period of three hours; the brown reaction mixture was stirred for another half hour at room temperature. It was then poured into a beaker containing 50 g. of crushed Dry Ice. The acidic material was extracted with 10% potassium hydroxide. The crude acidic fraction, 1.5 g. (7% yield), had a m.p. of 135–155°; it was dissolved in 10% sodium hydroxide, decolorized, acidified and then recrystallized from aqueous acetic acid (80%) to give 1.3 g. of long colorless needles, m.p. 158.5–160.5°; the reported⁶ m.p. of *trans*-stilbene-2-carboxylic acid is 158–160°. The infrared curve has a band at 10.35 μ as expected for a *trans* isomer.

From the neutral fraction there was recovered 15 g. of *cis*-2-chlorostilbene (identified by its infrared curve); a small amount of solid material was also obtained which on crystallization from methanol gave 0.2 g. of colorless needles, m.p. 117–120°. This is impure *trans*-stilbene; the reported m.p. of stilbene is 124°.

(2).—Fifteen grams of recovered *cis*-2-chlorostilbene was again treated with lithium. The reaction mixture was refluxed gently throughout the reaction, and for 12 hours longer. The deep red solution was poured onto 50 g. of crushed Dry Ice and worked up as before. The crude acid was brown and rubbery. It was purified through its sodium salt and recrystallized from methanol, m.p. 156–160°; yield 1.6 g., 10%. A larger amount of the solid neutral material was obtained; on recrystallization from ethanol soft colorless plates, m.p. 123–124°, were obtained. The infrared curve was identical with that of the by-products of the previous run.

Acknowledgment.—We wish to express our appreciation to the National Science Foundation for a research grant.

(5) A. Klages and F. Tetzner, *Ber.*, **35**, 3970 (1902).

(6) S. Gabriel and T. Posner, *ibid.*, **27**, 2506 (1894).

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The Thermal Decomposition of 2-Phenoxybenzoyl Peroxide

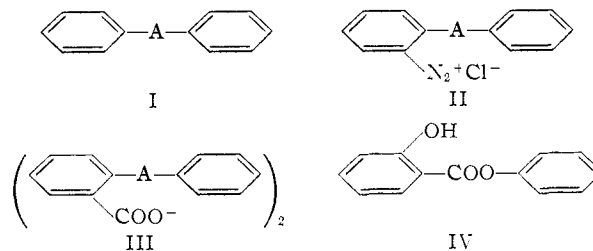
BY DELOS F. DETAR¹ AND ALEX HLYNSKY²

RECEIVED APRIL 7, 1955

In order to obtain information about the mechanisms of the reactions of free radical intermediates with aromatic rings, a number of compounds have been studied in which an intermediate free radical of structure I is expected. If the bridge group A is C=O or O, then an intramolecular free radical substitution reaction will lead to fluorenone or to dibenzofuran and the formation of the five-membered ring should exert an appreciable driving force in favor of ring closure. If A is a *cis*-ethylenic bridge,

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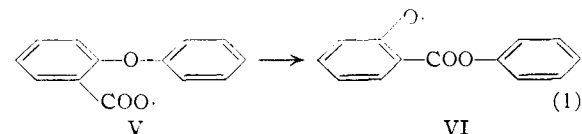
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then the ring closure to phenanthrene is perhaps even more favored. The two methods of producing the free radical intermediate I that seem to have been studied most thoroughly are the action of alkali upon the diazonium salt II or the thermal decomposition of the peroxide III.

Previous work³ has been carried out for the most part with the diazonium salts, for the desired peroxides have so far proved rather troublesome.

In the present work the peroxide of 2-phenoxybenzoic acid was obtained by treatment of the acid chloride in toluene with an aqueous solution of sodium peroxide. On thermal decomposition of the peroxide in benzene decarboxylation amounted to less than 1%. The major identified product was phenyl salicylate (IV), found in 25% yield. It is reasonable to consider that this product arises by cleavage of the peroxide to 2-phenoxybenzoyloxy radicals (V) which then undergo the intramolecular reaction (eq. 1) to give 2-(carbophenoxy)-phenoxy radicals (VI). This hypothesis has a certain amount



of supporting evidence: (1) the thermal decomposition appears to afford no anomalous behavior⁴; (2) the peroxide initiates vinyl polymerization; and finally (3) there seems reason to believe that ionic intermediates would give different products—the *o*-phenoxybenzoate anion should be inert, and the *o*-phenoxybenzoyloxy cation should rearrange⁵ to give an *o*-hydroxydiphenyl ether derivative.

The other reaction products of the thermal decomposition in benzene were a high-melting acid, possibly a dimer of 2-phenoxybenzoic acid (9%); 2-phenoxybenzoic acid (8–12%); ether-insoluble red tar (6%, by weight); unidentified acidic components (18%); neutral components insoluble in ethanol (30–40%). The phenyl ester of phenylsalicylate appeared to be absent.

Attempts were made to modify the phenyl salicylate yield by carrying out the decomposition in other solvents. The peroxide is not very soluble in isoöctane. In an isoöctane-carbon tetrachloride mixture (3:1 by volume) the phenyl salicylate yield was 19%; in chloroform the yield was 20%; and in a benzene-bromotrichloromethane mixture (88:22 by weight) the yield was 21%. The yield of this product was therefore insensitive to the solvents investigated.

(3) D. F. DeTar and D. I. Relyea, *THIS JOURNAL*, **76**, 1680 (1954); D. F. DeTar and Y. W. Chu, *ibid.*, **76**, 1686 (1954).

(4) A. T. Blomquist and A. J. Buselli, *ibid.*, **73**, 3883 (1951).

(5) J. E. LeMer, *ibid.*, **72**, 67 (1950).