

(7) F. Straus, *Ann.*, **342**, 190 (1905).

1- d_1 , give *cis* reduction (Table I). Palladium and cadmium activated zinc-acid reagents also give *cis* reduction (Table I).⁸

We believe that the *cis* products found with these metal-promoted zinc agents are evidence that the reactions are catalytic in nature. Palladium, with its unfilled d-band, is a conventional hydrogenation catalyst; copper has a filled d-band and pure copper films show no catalytic activity; however, technical copper hydrogenation catalysts are well known.⁹ Copper activated zinc and palladium activated zinc may be called *zinc-supported* catalysis.

Although zinc (cadmium) has a filled d-band and is not considered a hydrogenation catalyst, impure technique or commercial zinc, like copper, undoubtedly contains impurity centers which could account for such behavior. However, the *cis* reduction found with magnesium (Table I) renders more uncertain this interpretation of *cis* reduction by unpromoted zinc-acid.

Table I shows that the expected *trans* product arises by chemical reduction of acetylene- d_2 and propyne-1- d_1 . The stereochemical course of *chemical* reduction has been attributed to the greater stability (usually) of the *trans*-olefin product with respect to the *cis*-olefin.¹⁰ However, *chemical* reduction of dialkylacetylenes has been shown by Campbell and co-workers^{1b} to yield essentially 100% *trans*-olefins, whereas it is known that the *cis-trans* equilibria are by no means so far displaced.¹⁰ The present results indicate even more unequivocally that the thermodynamic properties of the possible products do not determine the course of reaction, since the *cis-trans* equilibrium constant for ethylene- d_2 has been found to be unity¹¹ while that for propene-1- d_1 must undoubtedly approximate unity.

Another mechanism of *trans*-addition has been advanced by Farkas and Farkas,^{1a} whereby chemical reduction proceeds *via* an intermediate,

$$\begin{array}{c} R_1 \\ \diagup \\ C \\ \diagdown \\ H \end{array} = \dot{C}R_2$$

or (I) whose configuration of minimum potential energy would be

$$\begin{array}{c} R_1 \\ \diagup \\ C \\ \diagdown \\ H \end{array} = \dot{C} \backslash R_2$$

atom of hydrogen to the intermediate is then postulated by these authors and by Campbell^{1b} to yield *trans* product. However, it appears that it is not (I) which governs the composition of the products. The latter is a rate-determined rather than equilibrium-determined result and depends upon the properties of the possible transition states which, for this mechanism, are not represented by (I). That this is so seems reasonable from the fact that for the case $R_2 = D = R_2$ no particular stereochemical configuration is favored by (I), whereas *trans* reduction is found. So (I) is not the transition state in this case. In general, postulation of transition states such as (I) for the Farkas mechanism of hydrogenation, or for other addition reactions, cannot be valid; since that would mean that the configuration of the products would be

independent of the size, or repulsive interaction with R_1 , of the entering group.

We are better able to say what is wrong concerning the mechanism of *chemical* reduction than what is correct. The mechanism(s) must be stereospecific. Possibly it involves electron donation to the substrate. Mechanisms have been suggested for sodium-ammonia reduction.¹² However, it does not seem worthwhile to speculate further. Detailed studies of the reduction with various agents would be desirable. We plan no further work on this problem.

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Experimental

Experiments were usually done in duplicate and sometimes in triplicate.

Materials.—Acetylene- d_2 was prepared as described previously⁶ and was of 99% isotopic purity. The D_2O used in the preparations was obtained on U. S. Atomic Energy Commission allocation.

Propyne-1- d_1 was obtained as follows. Propyne was prepared by bubbling acetylene to excess through a solution of 5 g. of sodium in liquid ammonia. The ammonia was evaporated to dryness to remove excess acetylene, which later proved troublesome, the liquid ammonia solvent was replaced and excess methyl iodide was slowly bubbled into the reaction mixture. The mixture was then evaporated to dryness while the gases passed through sulfuric acid bottles and finally through a liquid air trap. The condensed propyne was purified by distillation on a low temperature column of the Podbielniak type. The propyne was dissolved with a stoichiometric amount of sodium in liquid ammonia, the ammonia was evaporated and the sodium salt pumped under vacuum for 12 hours. A small excess of D_2O was slowly added dropwise and the evolved product was trapped and later purified by distillation. Infrared analysis showed approximately 10% of light propyne was present.

Tolane was obtained from Farchan Research Laboratories. Other reactants were reagent grade.

Analysis.—Deuteroethylene products were analyzed by means of their infrared spectra by the use of a Beckman IR-2 instrument. Intensities had been previously calibrated.⁸

Deuteropropene products were determined by examination of the infrared spectra of the products from 2 to 25 microns. We are indebted to Professor D. F. Eggers, Jr., for the KBr spectra. Both products showed a double bond band. The product from zinc (copper) reduction of propyne-1- d_1 showed some bands which were of different intensity and position from those obtained by chromous chloride reduction. The former material is assumed to be *cis*-propene-1- d_1 and the latter *trans*-propene-1- d_1 by analogy with the products obtained from other acetylenes with these reducing agents. The *cis* sample was isomerized and the spectrum of the sample altered precisely in the direction expected for appearance of the *trans* isomer. The details of the spectra will appear at a later date from this department.

Stilbene products were analyzed by running the infrared spectra of 0.5 *M* acetonitrile solution on a Perkin-Elmer Model 21 spectrometer. The spectra so obtained were compared with those of 0.5 *M* solutions of pure tolane, *trans*-stilbene and diphenylethane solutions in acetonitrile. Characteristic differences existed. The spectra of the products, however, were in every case identical with that of a product (*cis*) obtained by reduction of tolane with H_2 over Pd and agreed also with the spectrum of pure *cis*-stilbene recently published.¹³ Characteristic *trans* lines were absent in the products.

Zinc-Hydrochloric Acid Reduction of Acetylene- d_2 .—Five grams of zinc dust and 8 cc. of alcohol were frozen in a Pyrex

(8) I. G. Farbenind A.-G., French Patent 837,196, Feb. 3 (1939).

(9) H. S. Taylor, *Discussions Faraday Society* No. 8, 14 (1950).

(10) J. E. Kilpatrick, E. J. Prosen, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **36**, 559 (1946).

(11) N. R. Larson and B. S. Rabinovitch, unpublished results.

(12) K. W. Greenlee and W. C. Fernelius, *This Journal*, **64**, 2505 (1942); A. L. Henne and K. W. Greenlee, *ibid.*, **65**, 2021 (1943).

(13) D. S. Brackman and P. H. Plesch, *J. Chem. Soc.*, 2188 (1952).

tube with liquid nitrogen, 0.7 cc. of concd. hydrochloric acid was then poured in and the mixture was degassed by melting, freezing and pumping on a vacuum line. 10–15 cc. of acetylene- d_2 was admitted to the evacuated tube which was then sealed off. After one hour at room temperature, the tube was frozen, broken open on a vacuum line and the products trapped for analysis.

Magnesium-Hydrochloric Acid Reduction of Acetylene- d_2 .—The procedure here was similar to that for zinc reducing agent; however, the reaction was run at 0° for 10 min. The amount of reduction was considerably smaller than for zinc.

Zinc-Acetic Acid Reduction of Toluene.—Three grams of toluene was dissolved in 50 cc. of 95% acetic acid, 6 g. of zinc dust was added and the mixture was heated on a steam cone for two hours, in the absence of light. Two more successive 6-g. additions of zinc, with alternate heating on the steam cone, were made. Heating was then continued for 24 hours. When diluted with water, the solution became cloudy and some oil collected on the surface. The oil was removed with a medicine dropper, weighed and dissolved in acetonitrile. Unreacted toluene precipitated from the aqueous solution.

Zinc (Copper)-Acetic Acid Reduction of Toluene.—Three grams of toluene was dissolved in 50 cc. of 95% acetic acid and 1 g. of zinc dust, previously washed with 25 cc. of 10% CuSO_4 solution, was added. The mixture was heated on a steam cone for 2 hours when an additional 2 g. of zinc-copper dust was added and heating was continued. A third addition of catalyst, with subsequent heating for two hours, was made. The reaction mixture was cooled, diluted with water and the oil which collected on the surface of the solution was collected and dissolved in acetonitrile. The system was protected from light.

Zinc (Copper)-Water Reduction of Acetylene- d_2 .—The copper-activated reducing agent was prepared according to Straus.⁷ One gram of zinc-copper, 5 cc. of water and 15 cc. of acetylene- d_2 gas were frozen into a Pyrex tube, degassed by freezing and pumping several times and the tube was then sealed off. The tube was heated to 75° with occasional shaking for 1 hour, frozen, broken open on a vacuum line and the products pumped out and analyzed.

Zinc (Palladium)-Alcohol Reduction of Acetylene- d_2 .—The reducing agent was prepared by washing 5 g. of powdered zinc with 20 cc. of a 1% aqueous solution of PdCl_2 . The solid was filtered and washed three times with 10-cc. portions of absolute alcohol. The catalyst was sucked dry. 2–5 g. of activated zinc, approximately 5 cc. of alcohol and 15 cc. of acetylene- d_2 gas were frozen into a Pyrex tube,

degassed by freezing and pumping several times and the tube was then sealed off. The tube was heated to 50° with occasional shaking for 30 minutes. The remaining procedure was similar to that for the zinc (copper) runs.

Zinc (Copper)-Hydrochloric Acid Reduction of Acetylene- d_2 and Propyne-1- d_1 .—0.4 g. of copper activated zinc, approximately 15 cc. of 1 N HCl and 15 cc. of acetylene- d_2 were employed in a manner similar to that described for zinc (copper)-water, except that a reaction temp. of 25° and reaction time of 1–10 hours were employed.

The procedure for propyne-1- d_1 was similar except that the experiment was scaled up fifteen-fold. The yield (percentage reduction) of propene-1- d_1 was very low and the product (12 cc.) was isolated by distillation on a low temperature column.

Magnesium (Copper)-Hydrochloric Acid Reduction of Acetylene- d_2 .—The procedure employed was similar to that for zinc (copper) except that the reaction time was 30 min.

Sodium-Ammonium Reduction of Acetylene- d_2 .—Ten cc. of 1–3 N sodium-ammonia solution was placed in a Pyrex tube and the mixture was degassed by freezing in liquid nitrogen and pumping several times. Approximately 15 cc. of acetylene- d_2 gas was then admitted, the tube was sealed off and heated to –35° where it was kept for 30 minutes, with occasional shaking. The sample tube was then frozen, opened and the ammonia removed by passage of the gases through 1 N sulfuric acid; the acetylene was trapped in liquid nitrogen and subsequently analyzed.

Magnesium-Ammonia Reduction of Acetylene- d_2 .—Large excess of magnesium powder in 10 cc. of liquid ammonia with 15 cc. of acetylene- d_2 failed to give reduction during 2 hours at 0°.

Magnesium-Ammonia (Ammonium Chloride) Reduction of Acetylene- d_2 .—0.5 g. of magnesium powder and 0.6 g. of ammonium chloride were placed in a Pyrex tube and evacuated. Ten cc. of liquid ammonia was condensed in, followed by 10 cc. of acetylene- d_2 gas. The tube was sealed off and kept for one hour at –35°. The tube was then frozen, cracked open and the same procedure for product recovery followed as for sodium-ammonia.

Chromous Chloride Reduction of Acetylene- d_2 and Propyne-1- d_1 .—The reduction of acetylene- d_2 was carried out in the manner described elsewhere.⁶ The same procedure was followed for propyne-1- d_1 ; however, in this case the percentage reduction was relatively very small and the product was purified and isolated by distillation on a low temperature column.

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The Preparation of Substituted Benzilic Acids

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The preparations of thirty-two methyl-, methoxy- and phenyl-substituted benzilic acids are described. The characteristics of these as well as of certain intermediate aldehydes, benzoines and benzils are tabulated.

In connection with work on the kinetics of hydrogenation of phenyl groups, it became desirable to synthesize certain substituted benzilic acids. A number of these acids as well as some of the intermediates used in their preparation are previously unreported compounds. The purpose of this paper is to describe the synthesis of these substances and to record certain of their physical constants.

Experimental Part

A. Preparation via the Benzilic Acid Rearrangement.—The substituted benzaldehydes listed in Table I were prepared by the Sommelet reaction of the corresponding chloro-

methyl- or bromomethyl-hydrocarbon with an aqueous alcoholic solution of hexamethylenetetramine. The details of this method are illustrated by the following example.

Four moles of *o*-methylbenzyl chloride (562 g.) was added to a solution of 4.4 moles of hexamethylenetetramine (612 g.) in two liters of 60% aqueous ethanol containing 400 ml. of 37% formalin and the mixture was heated under reflux overnight. Most of the ethanol was removed by steam distillation, one liter of water was added, and steam distillation was continued until the distillate was free of oily droplets. The total steam distillate was diluted with twice its volume of water and extracted with ether. The ether extract was washed successively with dilute sulfuric acid, dilute sodium hydroxide and water, and then distilled. There was obtained 336–384 g. of *o*-tolualdehyde (70–80% yield), which boiled at 197–199°.