[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF WASHINGTON]

The Stereochemistry of Reduction of the Acetylenic Bond

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Zinc-acid reducing agents have been found to give *cis* reduction and not *trans* as generally accepted. Zinc-acid reducing agents promoted with metals such as copper and palladium, which also give *cis* reduction, are suggested to be of catalytic type and are termed *sinc-supported* catalysts. The *chemical* reduction of acetylene- d_2 yields *trans*-ethylene- d_2 and shows that the mechanism of reduction must be stereospecific. The stereochemistry of the *catalytic* and *chemical* reduction of the acetylenic bond is discussed and some current mechanisms are rejected.

The stereochemical course of the hydrogenation of disubstituted acetylenes, $RC \equiv CR$, has been studied by a number of workers.¹ The data are not as numerous as might be desired but as pointed out by Farkas and

but, as pointed out by Farkas and Farkas, they indicate consistent general behavior. *Chemical* reduction by means of agents such as alkali metal-ammonia, chromous ion solutions, etc., yields the *trans*-olefin; *catalytic* reduction with the common transition element catalysts, such as

platinum and nickel, proceeds by *cis* addition. These facts have been explained in a number of ways. It is the purpose of this paper to present some new experimental data, obtained in the course of other work, which bear on these questions and to point out that a number of hypotheses concerning the stereochemical course of reduction, which are current, cannot be correct.

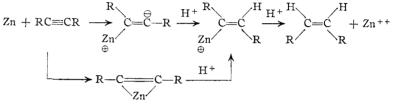
The results of the present study are summarized in Table I. Although chemical reduction of acetylenes by means of zinc-acid couples is believed to give trans reduction,^{1b} our results indicate otherwise. The evidence in favor of trans reduction is chiefly as follows. Aronstein and Holleman² found trans-stilbene and trans-cinnamic acid upon reduction of tolane and phenylpropiolic acid by zinc dust in acetic acid. Fischer³ obtained transcinnamic acid from phenylpropiolic acid with zinc dust in acetic acid. Liebermann⁴ isolated the same product by use of a zinc dust-alcohol combination. Finally Gonzales⁵ found trans reduction of stearolic and behenolic acids by zinc and acetic acid. In Table I, tolane is seen to give rise to cisstilbene so that the result of Aronstein and Holleman for this compound may be attributed to isomerization of the initially formed product. It is difficult to say whether the same conclusion applies to the reductions of the carboxylic acids just cited. Repetition of that work would be desirable. In any case, we also find *cis* reduction of acetylene- d_2 by zinc in alcoholic hydrochloric acid medium. Reduction of acetylene- d_2 by magnesium in the same medium proceeded *cis* as well.

There are two alternatives that would explain these findings. First, the reaction may conform to

(1) For reviews of the subject see: (a) A. Farkas and L. Farkas, Trans. Faraday Soc., 33, 837 (1937); (b) K. N. Campbell and B. K. Campbell, Chem. Revs., 31, 77 (1942); (c) G. W. Wheland, "Advanced Organic Chemistry." Second Edition. John Wiley and Sons, Inc., New York, N. V., 1949, p. 303.

(2) L. Aronstein and A. F. Holleman, Ber., 21, 2831 (1888); 22, 1181 (1889).

the *chemical* category, but unlike other *chemical* reductions involve some stereospecifically *cis* mechanism such as



The second alternative is that *cis* reduction of acetylenes by zinc-acid is actually *catalytic* reduction.⁶ Related to this question is the fact that copper-activated zinc-acid agents, as shown by Straus⁷ in the case of tolane and found here for tolane as well as acetylene- d_2 and methylacetylene-

TABLE I

STEREOCHEMICAL RESULTS OF THE REDUCTION OF SUB-STITUTED ACETYLENES

| STITUTED ACETYLENES | | |
|---------------------------|------------------------------|---|
| Reagent | Compound | Product |
| Zinc-1 N alcoholic HCl | Acetylene-d ₂ (A) | cis -Ethylene- d_2^a |
| Zinc-95% acetic acid | Tolane (T) | cis-Stilbene |
| Magnesium-1 N alcoholic | | |
| HC1 | A | cis-Ethylene-d2 ^a |
| Zinc (Cu activated)-water | Α | cis -Ethylene- d_2^a |
| Zinc (Pd activated)- | Α | 80% cis-Ethylene-d2 ^{a,b} |
| alcohol | | 20% trans-Ethylene-d2 |
| Zinc (Cu activated)-1 N | | |
| HCI | Α | cis -Ethylene- d_2 |
| Magnesium (Cu acti- | | |
| vated)-1 N HCl | Α | cis -Ethylene- d_2^a |
| Zinc (Cu activated)-95% | | |
| acetic acid | Т | cis-Stilbene |
| Zinc (Cu activated)-1 N | | |
| HC1 | Propyne-1-d ₁ (P) | cis-Propene-1-d1 ^c |
| Chromous chloride-acid | Α | $trans$ -Ethylene- d_2 |
| Chromous chloride-acid | Р | trans-Propene-1-d ₁ ^c |
| Sodium-ammonia | A | trans-Ethylene-d ₂ pre- dominantly ^d |
| Magnesium-ammonia | | |
| (NH ₄ Cl) | Α | $trans$ -Ethylene- d_2^e |
| Magnesium–ammonia | Α | No reduction |

^a Ethylene and ethylene- d_1 were also found in the products; they arise from exchange of acetylene- d_2 with the solvent, and are of no stereochemical significance. ^b The trans product is believed to arise from secondary reactions. Such behavior is found on hydrogenation catalysts; see reference 6. ^c See Experimental—Analysis. ^d Very extensive exchange of the original acetylene- d_2 and ethylene products was found; the ethylene- d_2 component of the products was predominantly trans. The cis-ethylene- d_2 found is believed to have arisen primarily by exchange and isomerization of the products of reduction. ^e Very extensive exchange of the original acetylene- d_2 and ethylene products was found; the ethylene- d_2 component was trans exclusively.

(6) See J. E. Douglas and B. S. Rabinovitch, THIS JOURNAL, 74, 2486 (1952), for discussion of the mechanism of catalytic hydrogenation leading to *cis* olefin formation.

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

⁽³⁾ E. Fischer, Ann., 386, 374 (1912); 394, 350 (1912).

⁽⁴⁾ C. Liebermann and H. Trucksass, Ber., 42, 4659 (1909).

⁽⁵⁾ A. Gonzales, Anales soc. españ. fis. y quím., 24, 156 (1926).

 $1-d_1$, 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 *chemi*cal reduction has been attributed to the greater stability (usually) of the *trans*-olefin product with respect to the *cis*-olefin.^{1c} 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 dis-placed.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, $\stackrel{R_1}{\underset{H}{\longrightarrow}}C=CR_2$

or (I) whose configuration of minimum potential

energy would be $_{H}^{R_{1}}C=C_{R_{2}}$. Addition of a second

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 equilibriumdetermined 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 pre-viously⁶ and was of 99% isotopic purity. The D₂O 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 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 pro-pyne 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 Labora-Other reactants were reagent grade. tories.

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.6

Deuteropropene products were determined by examina-tion 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 pro-pyne-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 chloride reduction. 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, transstilbene 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 H₂ 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-d2.-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 Acetylened₂.—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 Tolane.—Three grams of tolane 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 tolane precipitated from the aqueous solution.

Zinc (Copper)-Acetic Acid Reduction of Tolane.—Three grams of tolane was dissolved in 50 cc. of 95% acetic acid and 1 g. of zinc dust, previously washed with 25 cc. of 10% CuSO₄ solution, was added. The mixture was heated on a steam cone for 2 hours when an additional 2 g. of zinccopper 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.

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 PdCl₂. 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 Acetylened₂ and Propyne-1- d_1 .--0.4 g. of copper activated zine, 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, benzoins 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 chloromethyl- 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°.