

or allyl sulfide and a tertiary amine. Other quaternary salts undergo similar cleavage at higher temperatures in diethylene glycol solution.

Benzyltrimethylphenylammonium chloride is

rapidly cleaved by sodium hydrosulfite, yielding dimethylaniline and benzyltrimethylphenylammonium-S-benzylthiosulfate.

URBANA, ILLINOIS

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Hydrogenation of Substituted Acetylenes with Raney Nickel¹

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Other workers have shown that the course of the catalytic hydrogenation of substituted acetylenes is profoundly influenced both by the nature of the substituents and by the catalyst employed. With platinum catalysts,² in general, there is no change in the velocity of hydrogenation when two atoms of hydrogen have been absorbed, while with the less active palladium catalysts,^{2,3} there is frequently a great diminution in velocity, and it is possible to isolate the intermediate olefin in a pure state.

In this connection, it seemed of interest to study the catalytic hydrogenation of substituted acetylenes, using Raney nickel as the catalyst. Dupont⁴ has made a similar study, which was, however, limited to 1-heptyne, phenylacetylene, 2-octyne and 1-methoxy-2-nonyne. He reported that the two monosubstituted acetylenes showed little or no change in velocity of reduction when one molar equivalent of hydrogen had been absorbed, but that the disubstituted ones did.

We have extended the investigation to include mono- and dialkylacetylenes, mono- and diphenylacetylenes, and phenylmethylacetylene, in order to determine the effect of substitution on the course of the reaction. We have found that all the acetylenes studied are readily reduced at room temperature, and pressures of three to four atmospheres, and that at the beginning, at least, the reaction is markedly exothermic.

Our results show a relation between the symmetry of the acetylene molecule and the course of the reduction. The reduction curves for the monoalkylacetylenes showed a slight change in

slope at half reduction, while the dialkylacetylenes showed a more pronounced change in slope, which was particularly noticeable in the case of the symmetrical dialkylacetylenes. Phenylacetylene and phenylmethylacetylene, which are electronically the least symmetrical of the acetylenes studied, showed no change in slope in the reduction curve at half reduction. Diphenylacetylene, on the other hand, readily absorbed one molar equivalent of hydrogen, and the reaction stopped at this point, yielding isostilbene.

By stopping the reduction when one molar equivalent of hydrogen had been absorbed, it was possible to isolate the corresponding olefin in most cases. Raney nickel seems, therefore, to act catalytically similarly to palladium, and is easier to use. This appears to be a good method for preparing many pure olefins, with the double bond in a definite position, which are not readily obtainable by other methods. When the reduction is carried to completion, pure saturated hydrocarbons are obtained. Analyses made on the crude half-reduction products from the monoalkylacetylenes showed that less than 0.5% of acetylene remained. Since the acetylene used up accounts for practically all of the hydrogen absorbed, it is evident that very little saturated hydrocarbon was present. The physical constants of the 1-hexene and 1-heptene obtained by us compare favorably with those recorded in the literature. The method of analysis was not applicable to the products from the dialkylacetylenes, but since these showed a more pronounced change in slope in the reduction curve than did the monoalkylacetylenes, it is justifiable to assume that the olefins obtained are not appreciably contaminated by acetylenes or paraffins. Dupont⁴ showed by means of Raman spectra that the olefins obtained by the half-reduction of 2-octyne and 1-methoxy-2-nonyne contained little or no unreduced acetylene.

(1) Paper No. XXXV on the chemistry of substituted acetylenes; previous paper, *THIS JOURNAL*, **61**, 1462 (1939).

(2) Zalkind, *Z. physik. Chem.*, **104**, 177 (1923); Zalkind and Mokhnach, *J. Russ. Phys.-Chem. Soc.*, **62**, 1643 (1930); Ott and Schroeter, *Ber.*, **60**, 624 (1927).

(3) Bourguet, *Compt. rend.*, **180**, 1753 (1925); Gredy, *Bull. soc. chim.*, [5] **2**, 1029 (1935); Sherrill, *THIS JOURNAL*, **60**, 2562 (1938); Stoll and Rouve, *Helv. Chim. Acta*, **21**, 1542 (1938).

(4) Dupont, *Bull. soc. chim.*, [5] **3**, 1030 (1936).

No attempt was made in this work to establish the geometrical configuration of the olefins. Since Raney nickel seems to have a catalytic action similar to that of colloidal palladium, and since *cis* olefins are produced by the reduction of dialkylacetylenes with colloidal palladium,³ it seems reasonable to assume that the olefins obtained in this study had the *cis* configuration. This is supported by the fact that isostilbene was obtained from the half-reduction of diphenylacetylene.

Following the work of Reasenberg, Lieber and Smith,⁵ the promoting effect of small amounts of alkali and/or chloroplatinic acid on the catalytic reduction of amylacetylene and dibutylacetylene was investigated. When chloroplatinic acid and alkali were used together, reduction occurred more rapidly in the case of amylacetylene, but there was no significant change in the velocity of reduction of dibutylacetylene (see Fig. 2).

Experimental

Columns.—Unless otherwise noted, all distillations were made through a Fenske-Whitmore total-condensation, partial take-off column, packed with 3-mm. glass helices. The packed section was 12 mm. \times 400 mm.

Monoalkylacetylenes.—These were prepared from the alkyl bromides and sodium acetylide in liquid ammonia by the modified Picon synthesis,⁶ and purified by distillation through the column.

Dialkylacetylenes.—These were made from the alkyl bromides, sodamide and sodium acetylide by a modification of the procedure of Bried and Hennion.⁷ In the case of the unsymmetrical dialkylacetylenes, the higher alkyl group was introduced first.

Arylacetylenes. (a) **Phenylacetylene.**—This was made by a modification of the method described by Vaughn, Vogt and Nieuwland.⁸ Sodamide was prepared from 6 gram atoms of sodium in 2.5 liters of liquid ammonia, by the use of ferric nitrate as catalyst.⁸ Three moles of finely powdered, dry, styrene dibromide was added, with vigorous mechanical stirring, to the sodamide solution as rapidly as the reaction permitted. Stirring was then continued for two to three hours, after which the mixture was hydrolyzed with ammonium hydroxide and distilled water, and extracted with ether. The ether solution was washed with 15% hydrochloric acid to remove suspended iron oxides and dissolved ammonia, and then with a dilute solution of sodium carbonate and finally with distilled water. The dried solution was distilled *in vacuo* through the column to give 161 g. (52.5%) of phenylacetylene, b. p. 75° (90 mm.). We found this procedure more convenient than that described in "Organic Syntheses."⁹

(b) **Phenylmethylacetylene.**—Two moles of phenylacetylene was added to a solution of 2.2 moles of sodamide

in 2 liters of liquid ammonia. The solution was stirred for ninety minutes, and then 3 moles of dimethyl sulfate was added dropwise, with stirring, from a dropping funnel whose stem extended to the surface of the liquid ammonia. The mixture was stirred for about two hours, and was then worked up as described above. Fractionation of the product through the packed column gave 116 g. (50%) of phenylmethylacetylene, b. p. 113° (84 mm.).

(c) **Diphenylacetylene.**¹⁰—One mole of unsymmetrical diphenyldichloroethane¹¹ was added slowly to a solution of 3 moles of sodamide in 3 liters of liquid ammonia. The solvent was allowed to evaporate, and the solid residue was stirred with water to remove inorganic salts. The aqueous mixture was extracted with ether, the ethereal solution was washed with dilute hydrochloric acid, sodium carbonate solution and water. Distillation of the ether solution through a Claisen flask *in vacuo* yielded 142 g. (80%) of diphenylacetylene, b. p. 133° (8 mm.), m. p. 59°. The physical constants of the acetylenes used are recorded in Table I.

TABLE I
PHYSICAL CONSTANTS AND YIELDS OF SUBSTITUTED ACETYLENES

Acetylene	Yield, % ^a	B. p., °C.	Press., mm.	n_D^{20}	d_4^{20}	M_{RD} Obsd.	M_{RD} Calcd.
Butyl	60	71	745	1.3982	0.7140	27.67	27.71
Amyl	65	98	737	1.4087	.7285	32.56	32.42
Dipropyl	61	130	749	1.4249	.7573	37.13	37.04
Dibutyl	57	81	27	1.4330	.7698	46.53	46.32
Ethyl <i>n</i> -amyl	35	92	97	1.4295	.7616	42.01	41.70
Ethyl isoamyl ^c	35	87	99	1.4280	.7599	41.98	41.70
<i>n</i> -Pr-iso-Am ^c	35	104.5	97	1.4311	.7681	46.51	46.32
<i>n</i> -Bu- <i>n</i> -Am ^c	60	113	61	1.4360	.7760	51.21	50.93
Phenyl	53	75	90	1.5485	.9281	34.89	33.44
Phenyl methyl	50	113	84	1.5650	.9388	40.16	38.06
Diphenyl	80	133	8	M. p. 59°			
2-Me-2-hydroxy-3-octyne	50 ^b	102	48	1.4452	.8507	43.82	43.32

^a Based on the alkyl bromide used. In the case of the dialkylacetylenes, the yield is based on the alkyl halide of higher molecular weight. ^b Prepared from acetone and hexynylmagnesium bromide. ^c These compounds have not been reported previously.

Complete Reduction of Acetylenes.—A mixture of 3 g. of Raney nickel, prepared by the method of Covert and Adkins,¹² 0.2 mole of substituted acetylene and 100 ml. of absolute methyl alcohol was shaken with hydrogen in an apparatus similar to that described by Adams.¹³ Calibration of the apparatus with maleic acid showed that 0.1 mole of hydrogen corresponded to a change in pressure of 8.5 lb. (0.6 atm.). The initial hydrogen pressure was about 60 lb. per square inch (4 atm.). In all cases reduction was very rapid at first, and there was considerable liberation of heat. Reduction was usually complete in about thirty minutes. The saturated hydrocarbon was isolated by pouring the filtered solution into water, and distilling the dried organic layer through the packed

(10) This is essentially the method developed in this Laboratory by Dr. John Kroeger, and is a modification of that described by Maxwell, Doctoral Dissertation, Iowa State College, 1933.

(11) Buttenberg, *Ann.*, **279**, 324 (1894).

(12) Covert and Adkins, *This Journal*, **54**, 4116 (1932).

(13) Adams and Voorhees, "Organic Syntheses," Coll. Vol. 1, p. 53.

(5) Reasenberg, Lieber and Smith, *This Journal*, **61**, 384 (1939).

(6) Hennion, *Proc. Indiana Acad. Sci.*, **47**, 116-121 (1938).

(7) Bried and Hennion, *This Journal*, **59**, 1310 (1937).

(8) Vaughn, Vogt and Nieuwland, *ibid.*, **56**, 2120 (1934).

(9) Hessler, "Organic Syntheses," Coll. Vol. I, p. 428.

column. The results are recorded in Table II. The products gave negative tests for unsaturation with dilute aqueous alkaline potassium permanganate solution and with bromine in carbon tetrachloride.

TABLE II

PHYSICAL CONSTANTS AND YIELDS OF SATURATED HYDROCARBONS

Hydrocarbon	Yield, %	B. p., °C.	Press., mm.	n_{20}^D	d_{20}^4	MR_D Obsd.	MR_D Calcd.
<i>n</i> -Hexane	85	68	745	1.3763	0.6591	29.96	29.81
<i>n</i> -Heptane	74	96.5	753	1.3883	.6835	34.55	34.53
<i>n</i> -Octane	70	125	747	1.3987	.7039	38.71	39.14
<i>n</i> -Nonane	57	149.6	745	1.4055	.7173	43.79	43.76
<i>n</i> -Decane	75	173.2	745	1.4122	.7301	48.63	48.38
Ethylbenzene	84	136	745	1.4948	.8663	35.67	35.54

From the data obtained during the reduction (see Table III) curves were plotted showing moles of hydrogen absorbed against time in minutes. Typical curves are

TABLE III

REDUCTION DATA FOR SUBSTITUTED ACETYLENES

Moles of hydrogen absorbed by acetylenes^a

Time, min.	Butyl	Et <i>n</i> -Am	Dipropyl	Phenyl	Phenyl-methyl	2-Me-2-hydroxy-3-octyne
1	0.047	0.059	0.035	0.035	0.118	0.024
2	.141	.150	.129	.071	.235	.090
3	.188	.212	.188	.130	.282	.165
4	.235	.247	.200	.188	.318	.200
5	.259	.271	.212	.235	.341	.224
10	.318	.341	.260	.337	.365	.318
15	.353	.364	.294	.364	.377	...
20	.377	.377	.320	.370	.377	.353
25	.40	.40	.340	.377	.382	.365
30	.40	.40	.353	.377	.382	.365

^a In each case 0.2 mole of substituted acetylene was used.

shown in Fig. 1. The curves obtained showed that for the symmetrical dialkylacetylenes and the acetylenic

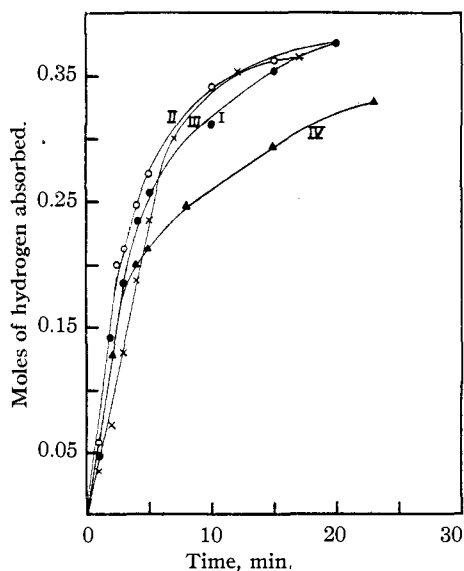


Fig. 1.—●, I, Butylacetylene; ○, II, ethyl-*n*-amyl-acetylene; ×, III, phenylacetylene; ▲, IV, dipropylacetylene.

carbinol there was a sharp change in velocity at half reduction. The change in velocity was less marked, although still definite, with the unsymmetrical dialkylacetylenes and the monoalkylacetylenes, but in the case of phenylacetylene and phenylmethylacetylene there was no appreciable change in velocity at half reduction. The reduction of diphenylacetylene, which was carried out in benzene solution because the substance is not sufficiently soluble in methyl alcohol, stopped when one molar equivalent of hydrogen had been absorbed, and the product isolated was identified as isostilbene.

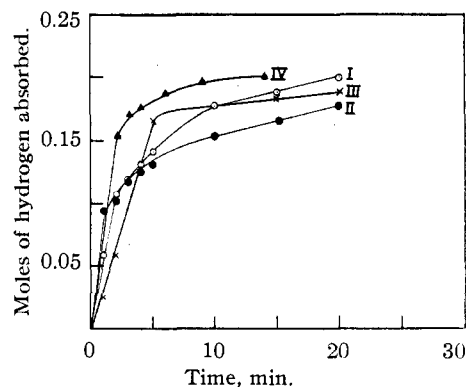


Fig. 2.—○, I, Unpromoted dibutylacetylene; ●, II, dibutylacetylene with alkali and chloroplatinic acid; ×, III, unpromoted amylacetylene; ▲, IV, amylacetylene with alkali and chloroplatinic acid.

Half Reduction of Acetylenes.—The half reductions of the substituted acetylenes were carried out as described above, except that the reaction was stopped when one molar equivalent of hydrogen had been absorbed. This usually required from two to five minutes, whereas in complete reduction the absorption of the second equivalent of hydrogen required fifteen to thirty minutes. Two 0.2-mole runs were combined, and the olefin isolated as described for the saturated hydrocarbons. The properties and yields of the olefins obtained are recorded in Table IV. In the case of styrene, the material tended to polymerize on distillation, and did not give satisfactory physical constants.

In order to determine whether appreciable amounts of substituted acetylene remained when one molar equivalent of hydrogen had been absorbed, analyses were made on the half reduction products of the monoalkylacetylenes. The methyl alcoholic solution from the reduction was filtered to remove the catalyst, diluted to 250 ml. with methyl alcohol and a 10-ml. portion taken for analysis. The sample was treated with 15 ml. of a 2% aqueous solution of silver nitrate, and the nitric acid liberated was titrated to the methyl red end-point with 0.05 *N* sodium hydroxide.¹⁴ The results showed that, in general, at half reduction less than 0.5% of monoalkylacetylene was present before fractionation.

Effect of Promoters.—Following the work of Reasenber, Lieber and Smith,⁵ the promoting effect of alkali

(14) This method has been in common use in this Laboratory for several years.

TABLE IV
 PHYSICAL CONSTANTS AND YIELDS OF OLEFINS

Olefin	Yield, %	B.p., °C.	Press., mm.	n_D^{20}	d_4^{20}	M_{RD} Obsd.	M_{RD} Calcd.
1-Hexene ^b	27	63	742	1.3862	0.6740	29.29	29.44
1-Heptene ^b	77	93	748	1.3990	.7004	33.84	34.06
4-Octene ^c	66	127.0	746	1.4128	.7184	38.86	38.68
3-Nonene ^c	74	147.4	750	1.4173	.7294	43.49	43.30
5-Decene ^c	77	169.6	746	1.4249	.7385	48.47	47.91
7-Me-3-octene ^c	77	140.7	746	1.4168	.7278	43.37	43.30
8-Me-4-nonene ^c	70	163.2	746	1.4229	.7400	48.18	47.91
5-Undecene ^c	86	191.2	750	1.4295	.7516	52.88	52.53
Isostilbene	87	133	8	1.6083	1.0143	60.73	59.18
2-Me-2-hydroxy- 3-octene	50	99.4	50	1.4427	0.8387	44.84	45.92
β -Me-styrene	50	166.7	746	1.5420	.9088	40.89	39.69

^a All boiling points except that for isostilbene were determined by means of the micro-Cottrell apparatus of Willard and Crabtree, *Ind. Eng. Chem., Anal. Ed.*, **8**, 79 (1936). ^b Schmitt and Boord, *THIS JOURNAL*, **54**, 751 (1932), record the following data: 1-hexene, b. p. 64° (760 mm.), n_D^{20} 1.3858, d_4^{20} 0.6732; 1-heptene, b. p. 95° (760 mm.), n_D^{20} 1.3999, d_4^{20} 0.6993. ^c These olefins have not been described previously.

and chloroplatinic acid were investigated in the reduction of amylacetylene and dibutylacetylene, as typical examples of mono- and dialkylacetylenes. In the case of amylacetylene, there was no promoting effect when chloroplatinic acid alone was used as promoter, but rather a slight retarding effect was noticed. When alkali and chloroplatinic acid were used together, there was some promotion observed (Fig. 2). In the case of dibutylacetylene, the use of alkali and chloroplatinic acid together resulted in no significant promotion (Fig. 2). The amounts of promoter, catalyst and unsaturated compound

used were the same as in the work of Reasenber, Lieber and Smith,⁵ but the pressure was about four atmospheres, rather than one atmosphere.

 TABLE V
 ANALYTICAL DATA FOR THE NEW OLEFINS AND
 ACETYLENES

Compound	Calculated		Found	
	% C	% H	% C	% H
Et- <i>i</i> -Am-acetylene	87.01	12.99	86.95	13.13
Pr- <i>i</i> -Am-acetylene	86.87	13.13	86.71	13.31
Bu- <i>n</i> -Am-acetylene	86.77	13.23	86.58	13.45
4-Octene	85.62	14.38	85.45	14.61
5-Decene	85.62	14.38	85.80	14.55
3-Nonene	85.62	14.38	85.39	14.47
7-Me-3-octene	85.62	14.38	85.76	14.58
8-Me-4-nonene	85.62	14.38	85.89	14.42
5-Undecene	85.62	14.38	85.73	14.57

Summary

1. The reduction of mono- and disubstituted acetylenes in the presence of Raney nickel has been studied, and a relation shown to exist between the symmetry of the acetylene molecule and the course of the reduction.

2. Several new olefins have been prepared by the half reduction of dialkylacetylenes. The half and complete reduction of acetylenes by means of Raney nickel is a feasible method of preparing certain olefins and saturated hydrocarbons.

NOTRE DAME, INDIANA

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The Conversion of Starch to Crystalline Dextrins by the Action of a New Type of Amylase Separated from Cultures of *Aerobacillus macerans*¹

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It was first shown by Schardinger² that the cultivation of *Aerobacillus macerans* upon starch solutions produces a mixture of water-soluble dextrins, from which two distinct, non-reducing, crystalline compounds may be readily isolated. Subsequent work by other investigators has not demonstrated with certainty whether these crystalline dextrins represent comparatively simple components of starch itself, or whether they are formed as the result of synthetic activity of the living organism. In the latter case they would seem to be of little importance to the study of the constitution of starch. We now find, however,

that when *Aerobacillus macerans* is grown for several weeks upon a potato medium, and the culture fluid is then filtered through a Berkefeld N filter to remove the microorganisms, the filtrate contains an enzyme which will produce the Schardinger dextrins from starch rapidly, and in greater yield than has been previously reported. We infer from this fact that the crystalline dextrins are components of the starch structure, or are closely related to such components.

During the course of the action of the enzyme upon starch there is no significant change in reducing power or optical rotation. In the present study, therefore, the progress of the reaction was followed by measuring the rapid and substantial decrease in viscosity, and also by means of a

(1) Publication authorized by the Surgeon General, U. S. Public Health Service.

(2) F. Schardinger, *Zentr. Bakt. Parasitenk.*, Abt. II, **22**, 98 (1908); **29**, 188 (1911).