one hour, while the α-furyl ketone required twelve hours. Data for certain physical properties of the cyclohexanones are listed in Table I

Preparation of Spirohydantoins.—These compounds were synthesized by the method of Bucherer[10] except that the amount of cyanide was doubled when the substituted Δ^2-cyclohexenones were used. This increase is required since it has been shown[11] that hydrogen cyanide adds to an ethylenic linkage when the latter is conjugated with a carbonyl group, as in these Δ^2-cyclohexenones. Likewise, it has been demonstrated[12] that sulfurous acid and alkali bisulfites add to the ethylenic linkage of Δ^2-cyclohexenones just as hydrogen cyanide does. Hence, by preliminary treatment of these ketones with alkali bisulfite solution, sulfonic acids of the spirohydantoins were produced.

Preparation of 2,4-Dioxo-7-aminomethyl-9-ethyl-7-methyl-1,3-diazaspiro(4,5)decane.—This compound was prepared by the reduction of 6 g. of the corresponding cyano compound (2,4-dioxo-7-cyano-9-ethyl-7-methyl-1,3-diazaspiro(4,5)decane), which was dissolved in 100 cc. of anhydrous amyl alcohol and treated with 4.5 g. of metallic sodium according to the method of Suter and Moffett[13] for the reduction of cyano compounds to the corresponding primary amines. After reduction was complete, careful neutralization caused separation of 2 g. (33% yield) of crystalline material melting at 223°. Although a carbylamine test failed and a picrate could not be formed, the compound reacted readily with nitrous acid to form nitrogen. Hence, the compound was analyzed for primary amino nitrogen by the micro method of Van Slyke.[14]

Anal. Calcd. for $C_{12}H_{21}N_3O_2$: C, 60.22; H, 8.85; total N, 17.56; primary amino N, 5.85. Found: C, 60.04; H, 8.79; total N, 17.52; primary amino N, 5.76.

The spirohydantoins were found to be markedly more soluble in water and in alcohol than the cyano-spirohydantoins; both types are readily soluble in alkaline solution and are reprecipitated unchanged upon acidification. The spirohydantoin-sulfonic acids are very soluble in water and in alcohol, while their potassium salts are less soluble than the acids. However, treatment of the potassium sulfonate derivative of the α-furyl-spirohydantoin with strong acids resulted in decomposition.

Summary

1. Four substituted Δ^2-cyclohexenones were converted by means of interaction with potassium cyanide and ammonium carbonate, into spirohydantoins containing a cyano substituent.

2. From four substituted cyclohexanones were obtained the anticipated spirohydantoin derivatives.

3. A third type of spirohydantoin, containing a sulfonic acid grouping, was obtained by initial treatment of the Δ^2-cyclohexenones with alkali bisulfite solution followed by reaction with alkali cyanide and ammonium carbonate.

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[10] Bucherer and Lieb, *J. prakt. Chem.*, [2] **141**, 5 (1934).

[11] Knoevenagel, *Ber.*, **37**, 4065 (1904).

[12] Knoevenagel, *ibid.*, **37**, 4038 (1904).

[13] Suter and Moffett, THIS JOURNAL, **56**, 487 (1934).

[14] Van Slyke, *J. Biol. Chem.*, **16**, 121 (1913).

AUSTIN, TEXAS RECEIVED FEBRUARY 27, 1943

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

The Addition of Hydrogen to Multiple Carbon–Carbon Bonds. IV. The Electrolytic Reduction of Alkyl and Aryl Acetylenes[1]

BY KENNETH N. CAMPBELL AND ELDRED E. YOUNG

Practically no work has been reported in the literature on the electrolytic reduction of compounds containing carbon–carbon unsaturation unactivated by an adjacent carbonyl group. A few unsaturated acids such as oleic acid have been reduced electrolytically at nickel and copper cathodes, and the electrolytic reduction at a copper cathode of some acetylenic carbinols has been reported.[2] We have found no mention of attempts to reduce acetylenic or ethylenic hydrocarbons electrolytically except for the work of Billitzer,[3] who reduced acetylene gas at a platinized platinum cathode to ethylene, and of Laitinen and Wawzonek,[4] who reduced aryl substituted olefins and acetylenes at a dropping mercury electrode.

Wilson[5] has pointed out that electrolytic reduction of conjugated compounds such as sorbic acid at high over-voltage cathodes resembles reduction by dissolving metals, and presumably occurs by a similar mechanism, while electrolytic reduction at low over-voltage cathodes, such as nickel and platinum, resembles catalytic hydrogenation. In earlier papers from this Laboratory[6,7] we have shown that dialkylacetylenes can be reduced by sodium in liquid ammonia to the *trans*-olefins, while catalytic hydrogenation of the

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[1] Paper III, THIS JOURNAL, **63**, 2683 (1941). Paper XLV on substituted acetylenes and their derivatives; previous paper, *ibid.*, **64**, 1220 (1942).

[2] Campbell and Campbell, *Chem. Rev.*, **31**, 129 (1942).

[3] Billitzer, *Monatsh.*, **23**, 199 (1902).

[4] Laitinen and Wawzonek, THIS JOURNAL, **64**, 1765 (1942)

[5] Wilson, *Trans. Electrochem. Soc.*, **75**, 353 (1931).

[6] Campbell and Eby, THIS JOURNAL, **63**, 216 (1941)

[7] Campbell and Eby, *ibid.*, **63**, 2683 (1941).

acetylenes leads to the *cis*-isomers. It was of interest, therefore, to investigate the electrolytic reduction of acetylenes at the two types of electrodes.

It was found that reduction of acetylenic hydrocarbons proceeded readily at spongy nickel cathodes. Variations in temperature were found to have little or no effect on the current efficiency of the process. Below a rather small limiting value of the cathode current density, current efficiencies were found to approach 100%. Increase of the current density above this value was found to give only a slight increase in the amount of reduction taking place, resulting rather in the evolution of excess hydrogen from the cell. Above a small limiting value the concentration of depolarizer in the cathode compartment was found to have no effect on the current efficiency.

The reaction was carried out with 1-heptyne, 4-octyne, 5-decyne, phenylacetylene and tolane. With the exception of phenylacetylene, which yielded a mixture of styrene and ethylbenzene, the product in every case was pure olefin, and the olefins obtained from the dialkylacetylenes and from tolane were shown to have the *cis*-configuration. This supports Wilson's theory that electrolytic reduction at nickel and platinum cathodes is closely related to catalytic hydrogenation. 5-Decyne was also reduced at a copper cathode, but in this case the reaction was very slow and the yield of olefin poor.

No reduction of the aliphatic acetylenic hydrocarbons could be obtained at the high over-voltage cathodes; although attempts were made with cadmium, lead, and amalgamated lead cathodes.

Since reduction of acetylenes at spongy nickel cathodes resembles catalytic hydrogenation, attempts were made to reduce purely aliphatic olefins at this type of cathode, since they can be reduced by catalytic methods. No evidence of reduction could be obtained, however, even when Raney nickel catalyst was added to the catholyte portion.

Experimental

Preparation of Acetylenes.—The phenylacetylene and tolane were prepared by the methods of Campbell and O'Connor[8]; the alkyl and dialkylacetylenes were made by the modified Picon synthesis.[9] All the liquid compounds made or obtained in this work were purified by distillation through a Whitmore Fenske column, and their physical constants were determined as described earlier.

Apparatus.—A three-neck, 1-liter flask was used for most of this work; anode compartments, made by sealing round porous cups (Coors no. 700, size 03) to 15-mm. glass tubing, were inserted through the two side necks. The anodes were made of 16-gage platinum wire wound into spirals weighing 6 g. each.

Rotating cathode stirrers were constructed of 60-mesh electrolytic nickel gauze, 60-mesh electrolytic copper gauze, sheet cadmium rolled from C. P. sticks and sheet chemical lead. These cathodes were all 15 cm. in circumference and 6 cm. high.

A hydrogen gas coulometer similar to that described by Muller[10] was connected in series with the reduction cell whenever it was necessary to determine the current efficiency.

Solvents.—One of the most serious difficulties was the insolubility of alkylacetylenes in solvents which will conduct an electric current. For satisfactory results the acetylenes should be soluble to the extent of 10%, and the solution should have a specific conductance of 0.075 mho. The only two solvents found which met these requirements were 95% ethyl alcohol containing 10% of sulfuric acid, and 95% ethyl alcohol containing 10% of potassium hydroxide. The basic solution was oxidized to acetic acid in the anode compartments, and this necessitated frequent changing of the anolyte.

Reduction at a Nickel Cathode.—A nickel gauze cathode was coated with spongy nickel by plating in an ammoniacal nickel sulfate solution. It was then washed with water and alcohol, but was not allowed to dry before use. The electrolytic apparatus was assembled, using 500 ml. of 95% alcohol and 25 ml. of concentrated sulfuric acid as catholyte, and 6 *N* sulfuric acid as anolyte. A current of two amperes was passed through the cell until the amount of hydrogen evolving from the cell was equal to that liberated in the coulometer. One-fourth mole (34.5 g.) of 5-decyne was then added to the catholyte. The current was maintained at two amperes and readings of the current efficiency were taken at hourly intervals. The current efficiency was almost 100% at the beginning, but fell rapidly to 50%, where it remained until sufficient hydrogen had been absorbed to convert almost all the acetylene present to the olefin; it then fell to a very low value, and the reduction was discontinued. About sixteen hours of reduction were required.

The catholyte was poured into two volumes of water; the organic layer was separated, washed several times with water, and dried over anhydrous magnesium sulfate. Fractional distillation yielded 21 g. of *cis*-5-decene (see Table I); this is a 75% yield. In other runs the yields varied from 60–80%, and in no case could traces of the original acetylene or of the saturated hydrocarbon be detected. Changes in temperature from 20 to 80° were found to have no appreciable effect on the current efficiency; doubling the current flowing through the cell decreased the current efficiency by 50%. When a cathode was used which had not been plated with spongy nickel, reduction was extremely slow.

4-Octyne and 1-heptyne reduced smoothly at a spongy nickel cathode in acid solution to yield the corresponding

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[8] Campbell and O'Connor, THIS JOURNAL, **61**, 2898 (1939).

[9] Bried and Hennion, *ibid.*, **59**, 1310 (1937).

[10] Muller, "Laboratory Manual of Electrochemistry," Eng. ed., G. Routledge and Sons, London, 1931, p. 31.

TABLE I

REDUCTION OF ACETYLENES AT A SPONGY NICKEL CATHODE IN ALCOHOLIC SULFURIC ACID

Acetylene	Product	Yield, %	B. p., °C.	Press., mm.	n^{20}_D	d^{20}_4	F. p., °C.
5-Decyne	*cis*-5-Decene	75	73°	30	1.4253	0.7445	−111
			73^a	30	1.4252	.7445	−112
4-Octyne	*cis*-4-Octene	80	72	150	1.4139	.7212	−116
			73^b	150	1.4136	.7205	−118
1-Heptyne	1-Heptene	65	93	740	1.3978	.6945	
Phenyl	Ethylbenzene and styrene	..	76–78	80	1.5007–1.5461		
Diphenyl	*cis*-Stilbene	80	145	18	1.6265		

[a] Results obtained by Campbell and Eby[6] for *cis*-5-decene. [b] Results obtained by Campbell and Eby[7] for *cis*-4-octene.

olefins. The results are summarized in Table I. Reduction of phenylacetylene at a spongy nickel cathode yielded a liquid, b. p. 76–78° (80 mm.), n^{20}_D 1.5007–1.5461, which appeared to be a mixture of ethylbenzene and styrene. It gave no precipitate with ammoniacal cuprous chloride. Styrene dibromide, m. p. 72–73°, was obtained by bromination of the portion with the highest index of refraction. The reduction product from tolane was shown to be *cis*-stilbene, for when it was treated with a very small amount of benzoyl peroxide and hydrogen bromide, and exposed in a quartz test-tube to the rays of a quartz mercury vapor lamp for thirty minutes it was converted to *trans*-stilbene, m. p. 123–124°.[11]

Reduction at Other Cathodes.—Attempts to reduce 5-decyne at a copper cathode plated with spongy copper yielded largely unchanged 5-decyne, but about 0.5 g. of material was obtained of b. p. 74° (30 mm.), n^{20}_D 1.4260; this appeared to be *cis*-5-decene. No reduction of 5-decyne could be obtained at a spongy cadmium cathode, in acid or alkaline solution, nor at a lead cathode in alkaline solution. Attempts to reduce 5-decyne and tolane at an amalgamated mercury cathode in acid and alkaline solution were unsuccessful. No reduction of 5-decyne was obtained when a platinum cathode was used, even in the presence of "carriers" such as chromic sulfate.

Summary

It has been shown that alkyl and aryl acetylenes can be reduced at a spongy nickel cathode in acid solution. 5-Decyne, 4-octyne and diphenylacetylene yield the *cis*-olefins, phenylacetylene gives a mixture of ethylbenzene and styrene and 1-heptyne yields 1-heptene. No reduction occurs at cathodes of cadmium, lead, amalgamated lead or platinum; very little reduction occurs at a copper cathode.

NOTRE DAME, INDIANA RECEIVED FEBRUARY 5, 1943

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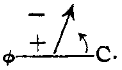
[11] Taylor and Crawford, *J. Chem. Soc.*, 2078 (1938).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF DUKE UNIVERSITY]

The Electric Moments of Some Substituted Benzoic Acids. II. The Moments of *o*-, *m*- and *p*-Fluorobenzoic Acids, and of *o*-Chloro and *o*-Bromobenzoic Acids

BY MARCUS E. HOBBS AND ARCHIE J. WEITH, JR.

Introduction

In the first paper[1] of this series the electric moments of the *meta*- and *para*-chloro and bromobenzoic acids were reported. It was pointed out there that apparently the resultant of the carboxyl group moment makes an angle of 72–76° with respect to the phenyl-carbon axis, *viz.*,  The present measurements of the three fluorobenzoic acids and of *o*-chloro and *o*-bromobenzoic acids were made in order to complete the chloro and bromo series, and to use the new fluoro series better to establish the value of the angle mentioned above. The fluoro acids were also of special interest to us since monomer-dimer equilibrium studies[2] by the dielectric polarization method had been carried out on these acids in this Laboratory. In the course of the above study the values of the electric moments of the unassociated acid molecules in benzene solution were calculated. We wished to compare the values thus obtained with those observed in dioxane solution where the acid molecule is hydrogen bonded to the solvent molecule.

Experimental

Dioxane.—Carbide and Carbon Chemicals Corp. dioxane, free from peroxides, was dried and refluxed with solid potassium hydroxide until discoloration practically ceased.

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(1) Brooks and Hobbs, THIS JOURNAL, **62**, 2851 (1940).

(2) Maryott, Hobbs and Gross, *J. Chem. Phys.*, **9**, 415 (1941).