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The Preparation and Properties of Certain Acetylenic Tertiary Carbinols

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The condensation of acetylene and simple monoalkyl acetylenes with aliphatic ketones has been investigated by a number of workers. Practical condensations have been effected with sodamide in ether,² calcium carbide-potassium hydroxide in ether,³ powdered potassium hydroxide in ether⁴ and sodium in liquid ammonia.⁵

The very high yields of carbinol obtained from tetrahydroionone and acetylene, using potassium *t*-amylate as condensing agent, by Gould and Thompson⁶ suggested the use of this condensing agent in the preparation of other acetylenic tertiary carbinols. The reaction was rapid and convenient and it was believed that in many cases the higher yields obtained would offset the higher cost due to the use of potassium. The method was naturally not applicable to the preparation of carbinols whose properties too closely resembled those of tertiary amyl alcohol. The condensation of acetylene with a number of simple ketones was carried out and the results are summarized in Table I. As can be seen from the table the yields were excellent in every case. All products were purified by distillation through a three-foot packed column. The unsaturated carbinols were characterized by quantitative hydrogenation of the triple bond; the values are included in Table I.

On attempting to condense *n*-butylacetylene with ketones, using potassium *t*-amylate, poor yields were obtained, under a variety of different conditions. Methods were worked out, however, for obtaining excellent yields, using hexynylmagnesium bromide. By collecting and measuring the volume of gas evolved during preparation of hexynylmagnesium bromide from hexyne-1 and ethylmagnesium bromide, an accurate estimate of the amount of Grignard reagent in the reaction mixture could be obtained (usually 85-90% of the amount theoretically derived from the ethyl bromide originally added). On adding the theoretic-

cal amount of ketone to react with the hexynyl magnesium bromide, yields of 85% of the tertiary carbinols were obtained (see Table I).

The acetylenic tertiary carbinols so obtained were submitted to the action of dehydrating agents in an effort to obtain the corresponding vinylacetylene derivatives. Interesting results were obtained on passing the carbinols over alumina at 230°. Under these conditions the hexynyl carbinols were dehydrated smoothly to give excellent yields of the corresponding vinylacetylene derivatives. With the ethynyl carbinols, however, the reaction took a different course, for on passing over alumina at 230° they were decomposed quite smoothly to yield the corresponding ketones and acetylene gas, only relatively small amounts of the dehydration products being obtained. Quantitative data for the behavior of the two types of carbinols are assembled in Table II. The decomposition of tertiary alcohols at elevated temperatures (400-600°) to yield hydrocarbons and ketones has been reported previously,⁷ and the decomposition of certain unsaturated secondary alcohols to yield olefins and aldehydes, when passed over alumina, is also known.⁸ However, the only reported description of the decomposition of dialkylethynylcarbinols into ketones and acetylene gas seems to be that of Locquin and Sung Wouseng.⁹

These authors reported such a decomposition on distillation of the acetylenic tertiary alcohols over platinum or palladium, but no experimental details are available.

Since dehydration over alumina was not satisfactory, the ethynylcarbinols were dehydrated in acetic anhydride containing sulfuric acid,¹⁰ which resulted in yields of 40-50% of the vinylacetylene derivative. Investigation of the vapor phase dehydration of these ethynyl carbinols is being continued with the hope of finding a dehydration catalyst which will not cause any abnormal reaction.

(1) Parts of the material in this paper were abstracted from theses submitted by John G. Burr, Jr., and E. N. Shaw to the Massachusetts Institute of Technology in partial fulfillment of the requirements for the degree of Bachelor of Science.

(2) Sung Wouseng, *Ann. Chim.*, [10] 1, 343 (1924).

(3) Kazarian, *J. Gen. Chem.* (U. S. S. R.), 4, 1347 (1934).

(4) Zakharova, *Sci. Repts. Leningrad State Univ.*, 2, 162 (1936).

(5) Campbell, Campbell and Eby, *THIS JOURNAL*, 60, 2882 (1938).

(6) Gould and Thompson, *ibid.*, 57, 340 (1935).

(7) (a) Grignard and Escourrou, *Compt. rend.*, 176, 1860 (1923); (b) Grignard and Chambret, *ibid.*, 182, 299 (1926).

(8) (a) Urion, *Ann. chim.*, [11] 1, 5 (1934); (b) Prévost and Ou, *Compt. rend.*, 206, 1661 (1938).

(9) Locquin and Sung Wouseng, *ibid.*, 174, 1551 (1922).

(10) Thompson, Milas and Rovno, unpublished results.

TABLE I

Acetylenic carbinol	% Yield		B. p., °C.	Press., mm.	n_D^{20}	Double bonds by cat. H ₂
	Calcd.	Isolated				
Methylethylhexynyl	92	78	118-121	760	1.4220	2.02
Methylpropylhexynyl	92.5	77	138-140	760	1.4282	2.03
Methylamylhexynyl	86	74	174-176	760	1.4362	1.99
Diethylethynyl	91.5	88	138-140	760	1.4366	2.03
Diisopropylethynyl	85	78	162-164	760	1.4492	1.97
Cyclohexylidineethynyl	90	90	81-83	18	1.4758	2.01
Methylethylhexynyl	49	44	105-110	25	1.4527	1.97
Methylpropylhexynyl	46	39	100-105	15	1.4529	2.01
Methylamylhexynyl	40	25	138-142	15	1.4534	2.01
By Grignard Synthesis						
Methylethylhexynyl		92	113-115	30	1.4525	2.01
Methylpropylhexynyl		91	123-125	30	1.4528	1.99
Methylamylhexynyl		87	140-142	15	1.4532	2.03

TABLE II

Acetylenic carbinol, 30 g.	Ethylyl-					Hexynyl-		
	Methyl-ethyl	Methyl-propyl	Methyl-amyl	Diethyl	Diiso-propyl	Methyl-ethyl	Methyl-propyl	Methyl-amyl
Vinylacetylene der.	Grams 4	4	Trace	2	0	22 ^a	22 ^a	21 ^a
	B. p., °C. 68-71	94-97	Odor	93-95	...	80-82 (30)	94-97 (30)	149-152 (30)
Ketone	Grams 10	12	15	15	22	1	2	3
	B. p., °C. 77-81	100-105	140-150	100-106	122-124	75-80	100-105	140-150
Ketone derivative	Compound Semicarb.	2,4-Dinit.	Semicarbazone	2,4-Dinit.	...	2,4-Dinit.	Semicarb.	...
	M. p., °C. { Obsd. 136	139	121	138	84	...	137	121
	{ Lit. 138	141	122	138	85	...	141	122
Carbinol								
Compound recovered	Grams 10	9	8	4.5	0	1	1	1
	B. p., °C. 110-120	135-140	165-175	128-136	...	70-75	70-75	70-80
C ₂ H ₂ Br ₄	Grams 44	46	40	60	69			
	n_D^{20} 1.6344	1.6346	1.6348	1.6348	1.6344			
C ₂ H ₂ , grams	3.3	3.5	3.0	4.5	5.2			
H ₂ O, grams	0.5	0.5	...	0.5	0	2.7	2.4	2.1

^a Analytical values for vinylacetylene derivatives obtained from the hexynyl carbinols.

	n_D^{20}	Formula	Carbon, %		Hydrogen, %		Hydrogen absorbed, cc.		
			Calcd.	Found	Calcd.	Found	G.	Calcd.	Found
1	1.4638	C ₁₀ H ₁₆	88.3	88.2	11.7	12.2	0.120	66	63
2	1.4642	C ₁₁ H ₁₈	88.0	88.3	12.0	12.1	.069	34	36
3	1.4662	C ₁₃ H ₂₂	87.6	87.7	12.4	12.5	.147	41	40

Experimental

Preparation of Dialkylethynyl Carbinols.—Ten grams of metallic potassium was dissolved in 120 cc. of *t*-amyl alcohol (dried by distillation from sodium). The solution of alkoxide was cooled to 0° and a vigorous stream of pure dry acetylene was passed through the solution, while one-quarter mole of ketone dissolved in 100 cc. of absolute ether was allowed to drop in. The solution was allowed to warm to room temperature, and stirring and passing in of acetylene were continued for three hours. The reaction mixture was poured onto a slight excess of iced dilute sulfuric acid, the organic layer separated, washed, and dried with magnesium sulfate. The ethereal solution of the carbinol was fractionated in a three-foot packed column with twenty-two theoretical plates. A preliminary fractionation was carried out to free the solution from most of the ether and any acetylenic glycol formed in the reaction. The entire middle fraction was then analyzed by quantitative catalytic hydrogenation, and the yield of car-

binol calculated. Under the conditions of the experiment it was the only substance present which would react with hydrogen. Further careful fractionation separated the acetylenic carbinol from the *t*-amyl alcohol. The purity of the acetylenic carbinol isolated was always checked by catalytic hydrogenation determinations. The yields in Table I were obtained in this manner.

Preparation of Dialkylhexynyl Carbinols.—The same procedure as described above was followed except that one-quarter mole of hexyne-1 was added to the amylate solution before the addition of ketone, and no acetylene gas was used. The yield was very low when the reaction was allowed to proceed at room temperature. When the reaction mixture was maintained at 70° for twelve hours larger yields were obtained, as reported in Table I, but the results were not considered satisfactory.

Better results were obtained by condensation of hexynylmagnesium bromide with the ketones as follows: 55 g. of ethyl bromide in 200 cc. of ether was added to 12 g. of

magnesium in 50 cc. of ether during one hour and refluxed one-half hour more. Forty-one grams of hexyne was then dropped in at such a rate that ethane was evolved smoothly. The evolved gas was collected and its volume determined, the amount varying between 10.3 to 10.8 liters (theory 12.5). Two hours were usually sufficient for the last gas bubbles to be evolved. 0.41 to 0.43 mole of ketone (corresponding to the amount of ethane evolved) was then added and the reaction mixture was heated an additional hour. On working up in the usual manner a yield of acetylenic carbinol over 85% was obtained in every case, based on the ketone used. The results are summarized in the lower half of Table I.

Decomposition of Acetylenic Carbinols over Alumina.—Standard conditions were developed for studying the reactions of the carbinols over alumina as follows. Thirty grams of carbinol was allowed to drop into a Pyrex tube 2.4×30 cm., filled with 8–14 mesh alumina and maintained at 230° in an electric furnace. It was established that the use of temperatures below 230° did not change the course of the reaction, but only the extent. The carbinol was swept through the reaction chamber in a stream of nitrogen. Two hours were sufficient to drive all the products into the receivers, the last of which was cooled with dry-ice. Acetylene gas was absorbed in three Emmerling towers kept saturated with bromine. The acetylene tetrabromide so formed was dissolved in carbon tetrachloride, washed free of bromine with bisulfite, and purified by vacuum distillation. From the weight of acetylene tetrabromide the weight of evolved acetylene was calculated. The liquid products were collected, the water separated and weighed, and the organic layer fractionated in an efficient Widmer column. Although an absolutely quantitative recovery was not possible, Table II furnishes quite an accurate picture of the course of the reaction. In most cases the recovered ketones were further characterized by the preparation of a derivative.

The vinylacetylene derivatives which resulted in excellent yields from the hexynyl carbinols were new com-

pounds. Since the hexynyl carbinols were derived from unsymmetrical ketones, the vinylacetylene fraction may consist in each case of two isomeric hydrocarbons.¹¹ No attempt was made to separate the two isomers but the hydrocarbon mixtures were analyzed by quantitative hydrogenation, and by elementary analyses¹² to establish their vinylacetylene character. The data are included in Table II.

Dehydration of Diethylethynylcarbinol with Acetic Anhydride.—Results for dehydration of this carbinol were typical of the series: 100 g. of carbinol was slowly dropped into 100 g. of acetic anhydride containing 1 g. of sulfuric acid. The temperature and rate of addition were maintained so that the substance distilled from the fractionating column below 110° . On washing free of acid, drying, and refractionating 31 g. of 3-ethylpentyne-1-ene-3 was obtained, b. p. $93\text{--}95^\circ$; yield 38%.

Summary

A number of acetylenic tertiary carbinols have been prepared. Ethynyl carbinols resulted in improved yields by condensation of ketones with acetylene using potassium *t*-amylate as condensing agent. Hexynyl carbinols were best prepared by use of hexynylmagnesium bromide. The decomposition of dialkylethynyl carbinols over alumina at 230° proceeded abnormally to yield acetylene and the ketone as the main products. With dialkylhexynyl carbinols, on the other hand, the normal products of dehydration resulted in excellent yields.

(11) Church, Whitmore and McGrew, *THIS JOURNAL*, **56**, 176 (1934).

(12) The authors wish to take this opportunity to thank Mr. Julius Kovitz who did the semi-micro carbon and hydrogen analyses included in this paper.

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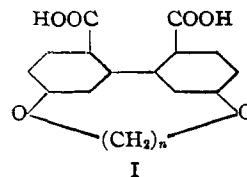
Stereochemistry of Biphenyls. LI. Resolution of Diphenic Acids Having Many-Membered Bridges Across the 5,5'-Positions: A Novel Type of Restricted Rotation¹

BY ROGER ADAMS AND NATHAN KORNBLUM

A large number of biphenyls, and related compounds, have been resolved.² In every instance, the required asymmetry has resulted from restricted rotation about a single bond produced by *ortho* substituents. The present investigation has been concerned with the production of restricted rotation by means of many-membered rings across the 5,5'-positions of diphenic acid, (I).

(1) For previous paper see Adams and Teeter, *THIS JOURNAL*, **62**, 2188 (1940).

(2) H. Gilman, "Organic Chemistry," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1938, p. 259.



Diphenic acid has been found to be incapable of resolution.³ There is a large body of evi-

(3) Kamm in C. S. Palmer's Thesis on "A Study of Optical Activity," University of Illinois, 1917; Bell and Kenyon, *J. Chem. Soc.*, 3044 (1926).