after cryst. from glacial acetic acid and methanol; mixed m. p. with tribromoquinaldine, prepared from quinaldine, 127.5–128.5°, showing their identity; yield, 2.9 g. crude product, m. p. 120–124°, or 88% of that calcd. (on the basis of the bromine used) from the equation

$$C_9H_6NCH_2COC_6H_5 + 3Br_2 = C_6H_5COBr + C_9H_6NCBr_3 + 2HBr$$

In a repetition, six equivalents of bromine were used, but the rate of addition was too rapid and some tar formed, which was removed readily with a stirring rod. The acetic acid solution was filtered and the precipitate washed with water to remove sodium bromide, leaving tribromoquinaldine.

To the filtrate 1.5 equivalents of aniline was added, and the solution shaken for about an hour at room temperature. The white precipitate, filtered and crystallized from methanol, was identified by m. p. and mixed m. p. as benzanilide (162.0–162.8°), yield 75%, which could only have been formed from benzoyl bromide. A little tribromoquinaldine was obtained by diluting the filtrate with water: total yield, 51%.

Phenacylquinoline dissolves readily in hot concd. hydrochloric acid, the hydrochloride separating in long almost colorless needles on cooling. This may be obtained, without solvent of crystallization, by passing hydrochloric acid gas through an ethereal solution of the ketone. The hydrochloride cannot be crystallized from water because it is hydrolyzed so readily. Phenacylquinoline is readily soluble in cold concd. sulfuric acid, and may be recovered unchanged by diluting the solution and neutralizing with ammonia. Picrate, precipitated in and crystallized from alcohol, yellow, m. p. 171.5–172.5° (uncorr.).

Summary

1. In agreement with the view that it is a cyclic ketone ether of the ammonia system, 2-methylquinoline (quinaldine) has been found to undergo a Claisen type condensation with many esters of aromatic acids in the presence of 2–3 equivalents of potassium amide. The following compounds have been prepared: 2-phenacylquinoline (benzoylquinaldine, α-quinolylacetophenone), *p*-bromophenacylquinoline, *o*-chlorophenacylquinoline, 2-furoylquinaldine, 2-*p*-methoxyphenacylquinoline, 2-*p*-methylphenacylquinoline, 2-phenacyl-4,5-benzoquinoline, 2-*p*-methoxyphenacyl-4,5-benzoquinoline, 2,3-diphenacylquinoxaline (?), 2-methyl-3-phenacylquinoxaline.

STANFORD, UNIV., CALIF. RECEIVED MAY 17, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Stereochemistry of Deuterium Compounds of the Type RR'CX_HX_D; Ethyl-d_4-ethylcarbinol

BY FRANK C. MCGREW[1] AND ROGER ADAMS

Research intended to investigate the asymmetry of a carbon atom of the type RR'CHD has been carried out by attempting to resolve cinnamic acid dideuteride,[2] succinic-α,α'-d_2 acid,[3] and by the preparation from optically active compounds of camphane-*d*,[4] camphane-2,3-d_2[5] and benzalacetone dideuteride.[6] In none of these experiments was the slightest indication of optical activity obtained.

The study of compounds of the type RR'-CX_HX_D, where X_H and X_D indicate groups identical but for one or more hydrogen atoms of one replaced by deuterium atoms in the other, represents an extension of the original problem which would answer equally well the question of the asymmetry conferred by hydrogen and deuterium symmetrically placed. It is possible, though incapable of theoretical demonstration, that such compounds in general would be much more likely to exhibit a measurable optical rotation than the type RR'CHD.

In the first example of the type RR'CX_HX_D, Clemo and McQuillen[7] found phenyl-d_5-phenylaminomethane after resolution to have a specific rotation [α] −5.7°, calculated from an observed rotation well beyond experimental error. An analogous compound, phenyl-d_5-phenylacetic acid, however, was found to be optically inactive when prepared from *l*-α-bromophenylacetic acid. Unsuccessful attempts to resolve the product with alkaloidal salts indicated that the inactivity was inherent and not due to racemization during formation.[8] Likewise, the activity found for cumene-*d*[9] was so slight that it is not beyond controversy.

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(1) This is a portion of a thesis submitted in fulfilment of partial requirements for the degree of Doctor of Philosophy in Chemistry. Chemical Foundation Fellow in Organic Chemistry.

(2) Erlenmeyer and Gärtner, *Helv. Chim. Acta*, **19**, 145, 331 (1936).

(3) Leffler and Adams, THIS JOURNAL, **58**, 1551 (1936).

(4) Biilmann, Jensen and Bak, *Ber.*, **69**, 1947 (1936).

(5) Leffler and Adams, THIS JOURNAL, **58**, 1555 (1936).

(6) Coppock and Partridge, *Nature*, **137**, 907 (1936).

(7) Clemo and McQuillen, *J. Chem. Soc.*, 808 (1936).

(8) Erlenmeyer and Schenkel, *Helv. Chim. Acta*, **19**, 1169 (1936).

(9) Burwell, Hummel and Wallis, *J. Org. Chem.*, **1**, 332 (1936).

TABLE I

PROPERTIES OF SUBSTITUTED ETHYLCARBINOLS

	$C_2H_5CHOH—R$ R =	Density$^{20}{}_4$			$n^{20}D$		MR_D					Boiling range	
		Found	Calcd.[a]	Lit.	Found	Lit.	Found	Calcd.[c]	$\alpha^{25}D$	l, dm.	$[\alpha]^{25}D$	Temp., °C.	Press., mm.
1	$CH{\equiv}C$—*d,l*	0.8859			1.4274		24.37	24.53				121.6–122.0	755
2	$CH{\equiv}C$—*l*	.8859			1.4276		24.39	24.53	−15.25	2	−8.38	121.4–122.0	750
3	C_2H_5—(red. of 1 with H_2)	.8217		0.8204[b]	1.4084	1.4103[b]	26.43	26.64				112.6–113.0	750
4	C_2H_5—(red. of 2 with H_2)	.8211		.8204[b]	1.4086	1.4103[b]	26.49	26.64	0.00	2	0.00	112.0–112.6	740
5	$CHD_2—CD_2$— (red. of 1 with D_2)	.8538	0.8579		1.4086		26.63					112.4–112.8	752
6	$CHD_2—CD_2$— (red. of 2 with D_2)	.8533	.8579		1.4081		26.62		.00	2	.00	111.8–112.4	740

[a] Calculated according to McLean and Adams, THIS JOURNAL, **58**, 804 (1936). [b] Timmermans and Henneaut-Roland, [*J. chim. phys.*, **29**, 529 (1932)]. [c] Calculated from Brühl's values.

The differences between the specific rotations of mandelic-O-*d* acid-*d*, phenyllactic-O-*d* acid-*d*,[10] and 2-octanol-O-*d*[11] and their hydrogen analogs might suggest intuitively that optical activity in the $RR'CX_HX_D$ type is to be expected. While such comparisons of the specific rotations of compounds of the types $RR'R''CX_H$ and $RR'R''CX_D$ are of some interest, there is no theoretical way, however remote, of relating the difference of rotatory power of these types to the question of the magnitude of the rotation of $RR'CX_HX_D$. Moreover, it is probable that the factors responsible for the difference between $RR'R''CX_H$ and $RR'R''CX_D$ are quite distinct from whatever qualities are necessary in X_H and X_D to enable them to confer asymmetry when substituted on the same carbon atom.

In the hope of obtaining the largest possible rotatory power from a compound in which X_H and X_D differed as greatly as possible, that is, in which X_D contained as many as possible D atoms relative to the weight of the group, the rotation of ethyl-d_4-ethylcarbinol was investigated. With ethylethynylcarbinol

$$CH_3—CH_2—CHOH—C{\equiv}CH \longrightarrow CH_3—CH_2—CHOH—CD_2—CHD_2$$

as a starting material, a partial resolution was effected by the phthalate method by repeated fractional crystallization of the brucine salt. A portion of the highly active ethylethynylcarbinol, $\alpha^{25}D$ −15.25°, thus obtained was reduced with hydrogen. The resulting diethylcarbinol had as pure liquid an observed rotation of αD 0.00 ± 0.01° in a 2-dm. tube. Another portion of the carbinol was reduced under identical conditions with deuterium; the ethyl-d_4-ethylcarbinol had in a 2-dm. tube an observed rotation αD 0.00 ± 0.01°.

The complete loss of optical activity upon reduction indicated that none of the activity of the *levo* carbinol was due to the presence of traces of methyl- or propylethynylcarbinol, either of which would have retained a detectable rotation. The inactivity was equally good evidence that the reductions as carried out were complete. In confirmation of this fact, the pure reduction products showed no trace of unsaturation in a test with permanganate so designed that the presence of 0.1% of unreduced carbinol was detected readily.

The purity of the active carbinol (compound 2) and its reduction products (compounds 4 and 6) was established by comparison of their physical properties with those of inactive ethylethynylcarbinol and its reduction products (compounds 1, 3 and 5) which were prepared on a larger scale (see Table I).

The authenticity of the diethylcarbinol prepared by the reduction of *d,l*-ethylethynylcarbinol with hydrogen was established by its physical properties and a derivative. The absence of any indication of impurity was evidence that the process of reduction did not initiate any rearrangement of the acetylenic compound. Thus, there is no reason to suspect rearrangement as an explanation for the loss of activity of *l*-ethylethynylcarbinol upon reduction, a fact further emphasized by the consistency of the physical properties of the reduction products.

Racemization of the unsaturated alcohol without rearrangement under the conditions of the reduction is extremely unlikely. For example, an analogous vinyl carbinol, active α-phenyl-α-methylallyl alcohol, has been reduced to methyl-β-phenylethylcarbinol without racemization.[12]

Incidentally, very little or no replacement of the

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(10) Erlenmeyer and Schenkel, *Helv. Chim. Acta*, **19**, 1199 (1936).

(11) Young and Porter, THIS JOURNAL, **59**, 328 (1937).

(12) Kenyon, Partridge and Phillips, *J. Chem. Soc.*, **85** (1936).

hydroxyl hydrogen by deuterium took place during reduction, for the infrared absorption spectrum of ethyl-d_4-ethylcarbinol had no perceptible maximum corresponding to the deuteroxyl group.[13]

From these results upon a compound whose group X_D has almost the highest deuterium concentration realizable, it must be concluded that the optical rotation of a compound of the type $RR'CX_HX_D$ is unlikely to be of measurable magnitude in a simple aliphatic case. The rotation observed by Clemo, if capable of substantiation, might then be explained by an unpredictable effect of the aromatic group.

In the absence of spectral and rotatory dispersion data through which use might be made of Kuhn's fundamental approach,[14] the only possible method of predicting theoretically the magnitude of the rotatory power is through the use of Boys' formula, which, since it is based on fundamental assumptions now considered hazardous, is highly questionable.[15]

To apply Boys' method to the optical rotation of a compound with hydrogen and deuterium symmetrically placed, it is necessary to calculate the atomic volume of deuterium relative to that of protium. Density data suitable for this calculation and sufficiently accurate to make it significant have been recorded for benzene-d_6.[16] The atomic volume thus obtained should be applicable to all benzene-d_x groups, although not necessarily to any others, since the densities of other deuterium compounds indicate that the atomic volume of deuterium may vary from slightly greater to slightly less than that of protium. The Boys calculation made in this way for phenyl-d_5-phenylacetic acid and for phenyl-d_5-phenylaminomethane predicts for both a specific rotation of the order of $[\alpha]$ 0.01°.

Experimental

Ethylethynylcarbinol.—One-half gram of hydrated ferric nitrate and 1 g. of sodium were dissolved in 1.5 liters of liquid ammonia and stirred until the blue color had turned to gray, indicating production of the iron catalyst.[17] Then 45 g. of sodium was added in a period of five minutes and the mixture stirred fifteen minutes more, or until the solution became gray. The flask was cooled to −50° with dry ice and a stream of dry acetone-free acetylene passed in for four hours, or until the solution became black. Then, with continued cooling to −50 to −60°, 116 g. of propionaldehyde was dropped in over a period of one hour. The solution was stirred for fifteen hours more, then the ammonia was allowed to evaporate. The mass remaining in a flask was treated with 107 g. of ammonium chloride dissolved in 1 liter of water and the mixture steam distilled. The product was salted out of the distillate with potassium carbonate, dried and distilled: b. p. 121–124° at 750 mm.; yield, 83.5 g. of colorless liquid (50% of theoretical) which became yellow on standing. Lespieau[18] reports b. p. 125° at 761 mm.

The 3,5-dinitrobenzoate was prepared by mixing the acid chloride with a pyridine solution of the carbinol and warming the mixture on a steam-bath for five minutes after letting it stand at room temperature overnight. The product was precipitated with water and dissolved in ether. The ether solution was washed successively with 1% hydrochloric acid, 1% sodium carbonate, and water, and evaporated to dryness. By recrystallizing the residue twice from 95% ethyl alcohol, glistening white needles were obtained, m. p. 91°.

Anal. Calcd. for $C_{12}H_{10}O_6N_2$: N, 10.07. Found: (Dumas): N, 10.30.

Ethylethynylcarbinol Hydrogen Phthalate.—Forty-two grams of ethylethynylcarbinol, 74 g. of phthalic anhydride, and 50 cc. of dry pyridine were heated in the absence of moisture for two hours on a steam-bath. The mixture was washed into a separatory funnel with ether, the pyridine extracted with 1 *N* hydrochloric acid, then the acidic substances extracted with 1 *N* aqueous ammonia. After washing the ammoniacal solution with ether, it was acidified and the oily acid ester extracted with chloroform. If any phthalic acid was suspended in the chloroform, it was removed by filtration. The chloroform was removed by evaporation, leaving a very viscous oil. When the oil was dried in a vacuum desiccator, it became vitreous and crystallized over a period of several days in massive prisms. The crystals were powdered in order to dry them completely. No solvent or temperature range tried was found effective for recrystallization, a heavy oil always being precipitated. The yield was 90.6 g. (78%), m. p. 72°.

Titration.—Subs. 0.1030 g. required 8.70 cc. of 0.0515 *N* sodium hydroxide. Calcd. for $C_{13}H_{12}O_4$: neut. equiv., 232.1. Found: neut. equiv., 230.0.

Resolution of Acid Ester.—The brucine salt was formed by dissolving 116 g. of ethylethynylcarbinol hydrogen phthalate and 197 g. of brucine together in hot dry acetone. By combining the product with four similar lots, a total of 1027 g. of salt was obtained for fractional crystallization. This process was complicated by a decomposition of the salt which caused the deposition of difficultly soluble dibrucine phthalate. The separation was carried out by the usual scheme through the fourth series of recrystallizations. At this stage, the least soluble portion, whose weight of 256 g. included some contaminating dibrucine phthalate, was decomposed by distributing between ether and 1 *N* hydrochloric acid. The ether solution was extracted with 1 *N* aqueous ammonia and the acid

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[13] This spectrum was kindly plotted by Dr. V. Deitz in the course of an investigation being carried out with Professors W. H. Rodebush and A. M. Buswell.

[14] Kuhn, *Z. physik. Chem.*, **B31**, 23 (1935), *et ante.*

[15] Boys, *Proc. Roy. Soc.* (London), **A144**, 655 (1934).

[16] Ingold, Raisin, Wilson, Bailey and Topley, *J. Chem. Soc.*, 915 (1936).

[17] Vaughn, Vogt and Nieuwland, THIS JOURNAL, **56**, 2120 (1934).

[18] Lespieau, *Compt. rend.*, **152**, 879 (1911).

ester isolated from the ammoniacal solution as in the preparation above. This acid ester was refluxed in 2 *N* aqueous sodium hydroxide for an hour, then the solution steam distilled. The *l*-ethylethynylcarbinol was salted out of the distillate with potassium carbonate, dried and distilled.

Reductions.—A modification of the apparatus described before[19] was used in which the reduction vessel had a capacity of 125 cc.

A solution of 3.8 cc. of *l*-ethylethynylcarbinol in 10 cc. of pure dry ethyl acetate was shaken with 0.08 g. of platinum oxide catalyst and hydrogen for twenty hours, during which time 1660 cc. (S. T. P.) of hydrogen was absorbed. Since the solution still showed a slight optical activity, indicating incomplete reduction, it was shaken for sixty hours more with hydrogen. The rotation of the solution had then dropped to zero and the product was removed from the solvent by fractional distillation through a 30-cm. column packed with a helix of nichrome wire having about three turns per cm. The same column was used in purifying all the other samples of carbinols.

The reduction of 4.7 cc. of the active carbinol in 15 cc. of ethyl acetate with 0.1 g. of catalyst and practically 100% deuterium was carried out in exactly the same way and used 1900 cc. (S. T. P.) of gas. The solution was slightly active after the first twenty hours and was shaken sixty hours more. The solution had then no detectable rotation. The product was isolated from the solvent by distillation as above.

One-tenth mole of *d,l*-ethylethynylcarbinol in ethyl acetate solution was reduced with hydrogen by the same procedure using 0.2 g. of catalyst. The product was isolated in the same way and its 3,5-dinitrobenzoate prepared by the procedure described for that of ethylethynylcarbinol. Glistening white needles were obtained, m. p. 99.0–99.5°.[20]

Anal. Calcd. for $C_{12}H_{14}O_6N_2$: N, 9.93. Found (Dumas): N, 10.03.

A pure sample of ethyl-d_4-ethylcarbinol was prepared by reduction of 0.1 mole of *d,l*-ethylethynylcarbinol with practically 100% deuterium and isolation in the same way. The 3,5-dinitrobenzoate prepared as above melted at 98.5–99.0°. A mixture of this derivative and that of diethylcarbinol showed no melting point depression.

Anal. Calcd. for $C_{12}H_{10}D_4O_6N_2$: N, 9.79. Found (Dumas): N, 9.45.

Summary

Ethylethynylcarbinol was partly resolved to give a *levo* form with high optical activity.

Reduction of this carbinol with hydrogen and with deuterium gave products polarimetrically indistinguishable in that neither had a detectable rotation in the pure state.

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[19] McLean and Adams, This Journal, **56**, 804 (1936).

[20] M. p. 97° given by Boese, Jones and Major, *ibid.*, **53**, 3530 (1931).

URBANA, ILLINOIS RECEIVED JUNE 14, 1937

[CONTRIBUTION NO. 34 FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

The Catalytic Reduction of Some Azo Compounds and its Application to the Identification of Azo Dyestuffs

BY WILLET F. WHITMORE AND ANTHONY REVUKAS

Introduction

The earliest catalytic reduction of an azo compound is that reported thirty-one years ago by Sabatier and Senderens.[1] They hydrogenated azobenzene in the vapor phase at 290° with a nickel catalyst and obtained chiefly aniline and small amounts of cyclohexylamine, dicyclohexylamine, and ammonia. Skita[2] got hydrazobenzene in five minutes and aniline in four and one-half hours with colloidal palladium under two atmospheres pressure. Brown and Henke[3] are patentees of a method for the reduction of azo and azoxy compounds with a nickel catalyst and hydrogen at 16.7 and at 33.3 atmospheres pressure and 100°, in which they claim good yields of the corresponding hydrazo compounds. More recently Winans and Adkins[4] have hydrogenated *p*-dimethylaminoazobenzene-*p*-sodium sulfonate at 100° and 100 atmospheres pressure, to *p*-sodium sulfanilate and *p*-dimethylaminoaniline within one hour over a nickel catalyst adsorbed on infusorial earth. With azobenzene, an ammonium carbonate type nickel catalyst on a kieselguhr support at 200° and 100–150 atmospheres pressure, they obtained 22% cyclohexylamine, 21% aniline, and 48% dicyclohexylamine in eight and one-half hours. At 90° a 95% yield of aniline was obtained within thirty minutes.[5] Andrews and Lowy[6] have investigated the catalytic reduction of azobenzene and *p*-aminoazobenzene in contact with platinum and with Raney nickel at 3 atmospheres pressure. They were interested primarily in the conditions

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[1] Sabatier and Senderens, *Bull. soc. chim.*, **35**, 259 (1906).

[2] Skita, *Ber.*, **45**, 3312 (1912).

[3] Brown and Henke, U. S. Patent 1,589,936, June 22, 1926.

[4] Winans and Adkins, This Journal, **54**, 311 (1932).

[5] *Ibid.*, **55**, 2056 (1933).

[6] *Ibid.*, **56**, 1411 (1934).