DL-*threo*-α,β-Diphenyl-β-hydroxyethylamine hydrochloride was prepared from the base (7.46 g.) by dissolution in ether (950 cc.) followed by addition of ethereal hydrogen chloride until the mixture was acid to congo paper. The product (8.1 g.) melted at 200–201°. It is much more soluble than the diastereoisomeric hydrochloride in mixtures of alcohol and ether.

N-Formyl-DL-*threo*-α,β-diphenyl-β-hydroxyethylamine was prepared from the hydrochloride by treatment with formamide and the product was isolated in the manner described for the *erythro* isomer; m.p. 145–146°; yield 93.5%.

Anal. Calcd. for $C_{15}H_{15}O_2N$: C, 74.66; H, 6.27; N, 5.81. Found: C, 74.71; H, 5.98; N, 5.97.

When boiled with 2.5 *N* HCl for 2 hours and the resulting solution was made alkaline, the free *threo* base was regenerated in high yields.

Attempts to isomerize the N-formyl derivative of the *threo*-hydroxyethylamine under the conditions used for the N-formyl-DL-*erythro*-α,β-diphenyl-β-hydroxyethylamine gave a 70% yield of DL-*threo*-α,β-diphenyl-β-hydroxyethylamine. Boiling the reaction mixture of the N-formyl-derivative and thionyl chloride for 1 and 2 hours followed by the regular work-up procedure gave 60 and 45% yields of the *threo*-hydroxyethylamine. Attempts to isolate the diastereoisomer failed.

N-Formyl-D-*erythro*-α,β-diphenyl-β-hydroxyethylamine was prepared in 88% yield by the formamide procedure. It separated from ethanol as fine needles; m.p. 203–204°. *Anal.* Found: C, 74.81; H, 5.83; N, 6.09.

N-Formyl-L-*erythro*-α,β-diphenyl-β-hydroxyethylamine was prepared in 70% yield (after recrystallization from alcohol) and obtained as lustrous needles from ethanol; m.p. 203–204°. *Anal.* Found: C, 75.00; H, 6.50. A mixture of approximately equal amounts of this product and its enantiomorph melted at 185–189°.

L-*threo*-α,β-Diphenyl-β-hydroxyethylamine.—N-Formyl-D-*erythro*-α,β-diphenyl-β-hydroxyethylamine (1.21 g.) was treated with thionyl chloride (2.5 cc.) by the method described for the racemate. The product, isolated in the same manner, melted at 114–115°; 89.6% yield. A solution in ether was converted to the hydrochloride by the addition of an ether solution of hydrogen chloride; m.p. 220–221°; $[\alpha]^{23}\text{D}$ +84.7° (*c*, 0.01, water). Treatment of the hydrochloride in water with excess sodium hydroxide precipitated the free base; m.p. 116–116.5°; $[\alpha]^{24}\text{D}$ 124° (*c*, 1.18, abs. alcohol).

D-*threo*-α,β-Diphenyl-β-hydroxyethylamine was prepared from N-formyl-L-*erythro*-α,β-diphenyl-β-hydroxyethylamine in the manner employed for its enantiomorph. The crude product, m.p. 114–115°, was obtained in 85% yield. By recrystallization from hot benzene, the product was obtained as rods; m.p. 115.2–115.8°; $[\alpha]^{22}\text{D}$ −123.7° (*c*, 1.2, abs. ethanol).[13]

Summary

1. The inversion of DL-*erythro*-α,β-diphenyl-β-hydroxyethylamine to DL-*threo*-α,β-diphenyl-β-hydroxyethylamine has been accomplished by treatment of the N-formyl derivative with thionyl chloride followed by acid hydrolysis of the intermediate oxazoline. The same inversion was applied successfully to the optically active forms of the DL-*erythro* series.

2. Configurations have been assigned to the four optically active isomers of α,β-diphenyl-β-hydroxyethylamine.

3. A new procedure for the resolution of DL-*erythro*-α,β-diphenyl-β-hydroxyethylamine using D-glutamic acid as the resolving agent is described.

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[13] Read, Campbell and Barker, *J. Chem. Soc.*, 2305 (1929), report m.p. 115.2°, [α]D +133° and −133° for the enantiomorphs. Ingersoll, THIS JOURNAL, **50**, 2264 (1928), reports [α]D +125° and −125.6° for the enantiomorphs.

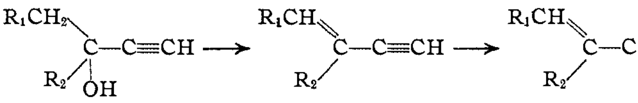
RAHWAY, NEW JERSEY RECEIVED AUGUST 31, 1950

[CONTRIBUTION FROM THE WEIZMANN INSTITUTE OF SCIENCE]

Dehydration and Isomerization of Dimethylethynylcarbinol

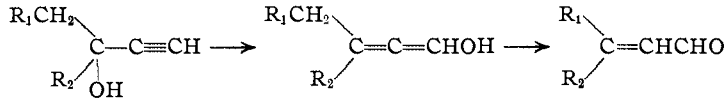
BY ERNST D. BERGMANN

The isomerization of acetylenic carbinols to carbonyl compounds has occupied a number of investigators who reported somewhat contradictory results.[1] It appears now that under the conditions used hitherto, ketones are formed almost exclusively, by dehydration of the tertiary carbinol group and hydration of the triple bond (*i.e.*, not by a true isomerization)[2]



I II III

Recently, Chanley[3] reported that 1-ethynyl-1-cyclohexanol gives a small amount (0.8–6%) of cyclohexylideneacetaldehyde in addition to the α,β-unsaturated ketone, 1-acetylcyclohexene. The mechanism of the aldehyde formation, which involves an allylic shift in a system containing a triple bond would be formulated as



I IV

The experiments reported here and intended to achieve the catalytic vapor phase dehydration of dimethylethynylcarbinol, are believed to shed some light on the phenomenon of its isomerization. It was observed that the dehydration is accompanied by isomerization and that in particular, an aldehyde, β,β-dimethylacrolein, is formed in constant and significant amounts.

Vaughn[4] has studied the **liquid-phase** dehydration of dimethylethynylcarbinol and has found concentrated sulfuric acid satisfactory, giving a 74% conversion and 57% yield, 3-methyl-3-butanol-2-one and methyl isopropenyl ketone (III, $R_1 = H$, $R_2 = CH_3$) being formed as by-products. 10% sulfuric acid gave a "quite low yield," phosphoric acid

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[1] For a survey of the literature, see E. Bergmann, "Acetylene Chemistry," Interscience Publishers, New York, N. Y., 1948, p. 60 ff.

[2] Hennion, Davis and Maloney, THIS JOURNAL, **71**, 2813 (1949).

[3] Chanley, *ibid.*, **70**, 244 (1948); see also MacGregor, *ibid.*, **70**, 3953 (1948); E. and F. Bergmann, *ibid.*, **59**, 1443 (1937).

[4] Vaughn, U. S. Patent 2,250,558 (*C. A.*, **35**, 7070 (1941)).

66% for 84.5% conversion. The latter acid gave a 12% yield from 3-ethyl-1-butyn-3-ol (I, $R_1 = R_2 = CH_3$), together with a considerable quantity of a ketone.[5] These results could not be wholly confirmed, concentrated sulfuric acid leading to a large amount of resins. 30% sulfuric acid proved to be the most useful concentration at a conversion of about 40%.

Vapor phase dehydration by means of the classical catalyst, activated alumina, was unsuccessful, the only reaction taking place consisting in the reversal of dimethylethynylcarbinol to acetylene and acetone.[6] Thoria on silica caused almost quantitatively the same breakdown as alumina, and converted part of the acetone further to mesityl oxide. Toluenesulfonic acid and phosphoric acid on the same carrier also gave side reactions to a considerable extent and the yields were not satisfactory (23.6% at 36% conversion, and 32.1% at 77.4% conversion, respectively). Eventually, ammonium phosphate was found to be suitable, which had been used for the conversion of 1,3-butyleneglycol into butadiene,[7] and in active carbon a satisfactory carrier was discovered, *i.e.*, a carrier which alone does not affect the dimethylethynylcarbinol.

Monoammonium phosphate is better than the diammonium salt. Both of them, when active carbon is imbibed with their solution, dissociate to a certain extent, leaving free ammonia in the solution. The rate of reaction, using these catalysts, becomes marked at about 200°, the best reaction temperature being 250°. Space velocities between 0.1 and 0.8 (liter dimethylethynylcarbinol per liter catalyst per hour) were found adequate. Alkali phosphates and ammonium and alkali arsenates proved unsatisfactory as dehydration catalysts.

Apart from unchanged starting material (and water), the reaction product consists of three compounds: isopropenylacetylene (II), methyl isopropenyl ketone (III) and β,β-dimethylacrolein (IV) which can be separated by fractionation (b.p.'s 35°, 100°, 135°, respectively; b.p. of dimethylethynylcarbinol (I) 105°). This is particularly easy if the reaction product is carefully dried: the unsaturated ketone (III) forms an azeotrope with water (b.p. 78–80°) as well as dimethylethynylcarbinol (I) (88–90°) and β,β-dimethylacrolein (IV) (b.p. 92–94°). In a typical run, in which a conversion of 99% was achieved, the following composition of the reaction product was determined; however, the composition varies somewhat with operating conditions

Water	12.0%
Isopropenylacetylene	44.0%
Methyl isopropenyl ketone	10.6%
Dimethylacrolein	28.2%
Higher-boiling material	5.2%

The high-boiling material was composed largely of the dimeride of methyl isopropenyl ketone.

The methods by which the various components of the reaction product were determined and identified, are described in the Experimental part. It is believed that the possibility of the formation of α,β-unsaturated aldehydes *and* ketones by isomerization of tertiary acetylenic carbinols has been proven, but no attempt has so far been made to verify whether the two isomerides of dimethylethynylcarbinol are formed independently, or whether they are also capable of interconversion. Such interconversions which almost evade formulation by means of the chemical reaction schemes, are not unknown,[8] and it is believed that the use of labeled atoms may contribute to the solution of this more intricate problem. As no hydration of (II) to (III) could be observed under our conditions, it seems doubtful whether the mechanism proposed by Hennion, Davis and Maloney[2] applies also to the vapor phase dehydration.

Thanks are due to the management of Publicker Industries, Inc., Philadelphia, for the permission to publish the above results which were obtained in their laboratories. The author was assisted in this work by Mr. R. Wilder and Drs. Dan Herman and Culver; their help and advice is gratefully acknowledged.

Experimental

The **liquid-phase dehydration** of dimethylethynylcarbinol was best conducted by adding 200 g. of dimethylethynylcarbinol gradually to a flask containing 300 g. of hot 30% sulfuric acid (initial temperature 95–100°). The vapors were separated continuously in a column, and distillation was continued, by gradually raising the temperature, until no more organic matter appeared in the distillate. The distillate consisted of 167 g. (212 cc.) of an oily and 65 cc. of an aqueous layer; the latter contained 16 cc. of organic material which was recovered by addition of anhydrous potassium carbonate (with cooling). A viscous resin (25.5 g.) had formed in the reaction flask. Fractionation of the combined and dried organic layers gave 116.5 g. of unchanged dimethylethynylcarbinol (conversion, 41.7%) and 59.1 of isopropenylacetylene (yield 90.0%, calculated on methylbutynol entered into reaction).

Vapor Phase Dehydration.—The vapor phase dehydration was carried out in a vertical quartz tube, which was electrically heated (automatic temperature control).

(a) **Catalysts.**—When 256 g. (500 cc.) of granular active carbon was kept in contact with a solution of 360 g. of diammonium phosphate in 740 cc. of water (total volume of the solution, 1 l.) for 24 hours, the weight increase of the solid (after drying) was 5%. Analysis of the supernatant liquid showed a ratio of NH_4:PO_4, 2:0.92, and correspondingly in the catalyst a ratio of 2:1.10 was found.

The affinity of the active carbon to monoammonium phosphate is greater: 250 g. of active carbon adsorbed 9% of its weight, when treated with a liter of the solution of the salt, containing 150 g. The molar ratio of NH_4:PO_4 in the supernatant solution was 1:0.83.

(b) **Products: Methyl isopropenyl ketone (III)** was identified in the appropriate cut by conversion into its 2,4-dinitrophenylhydrazone of m.p. 185–186°.[9] **β,β-Dimethylacrolein (IV)** boiled, upon redistillation, at 52–55° (40 mm.) and showed a density of 0.8781 and a refractive index of 1.4506. *Anal.* Calcd. for C_5H_8O: C, 71.4; H, 9.5; Br no., 190.5; *MR*, 24.84 (without exaltation). Found: C, 71.0; H, 10.0; Br no., 200; *MR*, 25.61. It was converted into the following characteristic derivatives.[10] A mixture of 4.2 g. of the compound and 7.7 g. of *p*-nitro**phenylhydrazine** in 50 cc. of butyl alcohol reacted with liberation of heat. The condensation was completed by refluxing the mixture for 1 hour. Upon cooling, violet crystals separated; from isopropyl alcohol, m.p. 161°, yield 7.5 g.

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[5] This is designated as 3-methyl-2-hexen-4-one. Obviously, the product should be 3-methyl-2-penten-4-one, provided the dehydration involves the ethyl and not the methyl group.

[6] Vaughn, U. S. Patent 2,197,956 (*C. A.*, **34**, 5461 (1940)), claims that "acidic activated alumina" gives a more satisfactory performance, if the conversion per pass is kept low (about 5%).

[7] Lorch, U. S. Patent 2,371,530 (*C. A.*, **39**, 3552 (1945)); Tollefson, U. S. Patent 2,373,153 (*C. A.*, **39**, 4774 (1945)).

[8] Venus-Danilova, *et al.*, *Ber.*, **59**, 377, 1032 (1926); *C. A.*, **42**, 110 (1948); Pines and Ipatieff, THIS JOURNAL, **69**, 1337 (1947).

[9] MacMahon, *et al.*, THIS JOURNAL, **70**, 2971 (1948).

[10] Fischer, Ertel and Loewenberg, *Ber.*, **64**, 30 (1931).

Both 4.2 g. of the compound and 5 g. of anhydrous potassium acetate were dissolved in methanol, and a solution of 5.6 g. of **semicarbazide hydrochloride** in water was added. From the clear solution, shiny leaflets began to crystallize immediately: from dioxane, m.p. 221° (dec.); yield 7 g.

Dehydration of 3,5-Dimethyl-1-hexyn-3-ol.—At a temperature of 300°, 167.5 g. of 3,5-dimethyl-1-hexyn-3-ol (b.p. 145°) was passed over 150 cc. of the active carbon diammonium phosphate catalyst in the course of one hundred and sixty-five minutes. The water layer (16 cc.) was separated and the organic layer dried and fractionated. The unsaturated hydrocarbon formed boiled at 100–110° (760 mm.); yield 40.5 g. (40%). Forty-six and one-half grams of starting material was recovered (28%), and 10 g. of a higher-boiling fraction (85–90° (5 mm.)) was obtained which has not been investigated further. The same applies to the considerable distillation residue.

The reaction product showed d^{20}_{4} 0.7519 and n^{20}_{D} 1.4274; (*MR*, found, 36.87; theory, 36.69 (without exaltation)); its analysis gave slightly too low carbon values, perhaps due to autoxidation. *Anal.* Found: C, 87.9, 87.6; H, 11.6, 11.4. Calcd. for C_8H_{12}: C, 88.9; H, 11.1. Whether the dehydration involved the methyl or the isobutyl group (or both), remains to be determined.

Summary

In the vapor phase dehydration of dimethylethynylcarbinol, the expected dehydration product isopropenylacetylene (II) is accompanied by two isomerization products: methyl isopropenyl ketone (III) and β,β-dimethylacrolein (IV).

The differences between liquid and vapor phase dehydration are emphasized and the reaction mechanism is discussed.

Rehovoth, Israel Received July 28, 1949

[Contribution from the Wm. H. Chandler Chemistry Laboratory, Lehigh University, and the Noyes Chemical Laboratory, University of Illinois]

Studies in the Sulfone Series. VIII. Infrared Absorption Spectra and Structure of Some Substituted Diphenyl Sulfones and Sulfoxides

By E. D. Amstutz, I. M. Hunsberger[1] and J. J. Chessick

It has recently been pointed out[2] that an interesting parallelism exists between aldehydes, C-nitroso compounds and sulfoxides on the one hand and acids (or esters), C-nitro compounds and sulfones on the other. In every case the substances in the lower oxidized state exhibit a chemical reactivity which is either lacking or greatly repressed in those in the higher oxidized condition. While no claim is made for the originality of this observation since it doubtless has been noticed by many others, it did suggest the possibility of an interesting solution to the vexing problem of the extreme stability of sulfones. This stability, which is usually taken for granted by chemical investigators, is so extraordinary that we believe it to be a characteristic of the system which is of prime importance. It would appear that since resonance is important in the stabilization of the carboxyl (and carbalkoxyl) and nitro groups it might be responsible likewise for the characteristic inertness of the sulfone structure.

The above parallelism likewise suggested a means of experimentally subjecting the concept to proof. It seemed necessary at the outset to demonstrate a difference between the oxygen to sulfur bond in sulfones and that in sulfoxides. This we have done by demonstrating that the sulfone and sulfoxide oxygen atoms differ considerably in basicity (proton binding power). Secondly, we were interested in determining whether these differences paralleled the known differences between aldehyde-type carbonyl oxygens and ester-type carbonyl oxygens.

It has previously been shown by several investigators that an aldehyde group situated ortho to a phenolic hydroxyl group forms a very strong H-bonded structure. The strong chelation is shown clearly by a shifting to a longer wave length of the characteristic fundamental band of the hydroxyl group in the infrared region of the spectrum. The peculiarly different carbonyl oxygen of the carbomethoxyl group forms a less strongly chelated system with the result that the hydroxyl shift is not as pronounced. A further important difference to be noted is that in salicylaldehyde the hydroxyl band is more diffuse and the maximum cannot be picked out with any degree of certainty (see Table II).

By extrapolating the above considerations it would seem probable that H-bonds of greater strength than that in salicylaldehyde would either give a more diffuse hydroxyl band or none at all in the region of the fundamental. As will be mentioned later this appears to be the case with *o*-hydroxydiphenyl sulfoxide and 1-nitroso-2-naphthol.

Because the infrared spectrum affords a picture of the molecule in its ground state[3] and because the measurements are precise and capable of registering small differences it seemed that the infrared examination of the strength of chelation in *o*-hydroxydiphenyl sulfones and sulfoxides by way of the OH shift might well afford the type of information desired. The present paper reports on the results obtained with a representative series of such compounds.

Experimental

Preparation of Materials.—The hydroxy and methoxy sulfones used in this work were prepared by a standard procedure which involved the synthesis of the nitrodiphenyl sulfide from thiophenol and a nitrochlorobenzene, oxidation of the sulfide to the sulfone and then replacement of the nitro group by hydroxyl by way of reduction, diazotization and hydrolysis. Since the method has been used before

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(1) Department of Chemistry, Antioch College, Yellow Springs, Ohio.

(2) Amstutz, Chessick and Hunsberger, *Science*, **111**, 305 (1950).

(3) Recent studies by Fehnel and Carmack, This Journal, **71**, 231 (1949); *ibid.*, **72**, 1292 (1950); Fehnel, *ibid.*, **71**, 1063 (1949); Koch, *J. Chem. Soc.*, 408 (1949); and Mathieson and Roberston, *ibid.*, 724 (1949), have dealt with the absorption of highly energized molecules (ultraviolet spectra). There is reason to believe (see Koch, *et al.*, *ibid.*, 2442 (1949)) that the conjugation revealed in the energized state by ultraviolet spectra is not characteristic of the ground state.