phthalic anhydrides has been known for over half a century.[2,3]

[2] Tiemann and Krüger, *Ber.*, **29**, 901 (1896).
[3] Fuller and Kenyon, *J. Chem. Soc.*, **126**, 2309 (1924).

DEPARTMENT OF CHEMISTRY
BATTERSEA POLYTECHNIC
LONDON S. W. 11, ENGLAND RECEIVED JANUARY 27, 1948

Rearrangement of Phenylethynylcarbinol

BY WARREN S. MACGREGOR

Rupe[1] reported that several tertiary acetylenic alcohols containing a free acetylenic hydrogen were rearranged upon boiling with 85% formic acid to the corresponding α,β-unsaturated aldehydes. Thus, the ethynylcarbinols from tetrahydrocarvone and fenchone were reported to yield 5 - isopropyl - 2 - methylcyclohexylidene - 1 - acetaldehyde and 1,3,3-trimethylbicyclo[2,2,1]-heptylidene-2-acetaldehyde, respectively.[2] The reaction represents a special case of a Meyer–Schuster rearrangement[3] and was considered by Rupe[1] to proceed in analogous manner

$$\mathrm{R(R')C(OH)C{\equiv}CH} \longrightarrow \mathrm{R(R')C{=}C{=}CHOH} \longrightarrow \mathrm{R(R')C{=}CHCHO}$$

Reinvestigation of several of the reported rearrangements by Fischer and Lowenberg,[4] Hurd and Christ[5] and others demonstrated that the principal products were unsaturated ketones presumably formed by dehydration of the carbinols followed by hydration of the triple bond.[5] Thus, 1-ethynylcyclohexanol yielded 1-acetylcyclohexene[4,5] rather than cyclohexylidene acetaldehyde. Chanley[6] showed that both the ketone and aldehyde products resulted from the rearrangement of 1-ethynyl-1-cyclohexanols although the aldehydes were formed in very low yield (0.8 to 6%).

The reaction probably involves initial elimination of the hydroxyl group to form a carbonium ion. The loss of a proton from an adjacent carbon followed by hydration of the triple bond and ketonization would yield the observed unsaturated ketone. Shifting of the carbonium ion bonds to the allenic structure followed by hydroxylation at the positive terminal carbon would yield the enolic form of the unsaturated aldehyde which is in equilibrium with the predominantly favored aldehyde.

A compound such as phenylethynylcarbinol would yield a carbonium ion that could not form an unsaturated ketone by the above mechanism and hence, barring alternative modes of reaction, should yield cinnamaldehyde as the principal rearranged product. When the carbinol was heated with 30% sulfuric acid, 85% phosphoric acid or phthalic anhydride the odor of cinnamaldehyde was evident but the material was largely polymerized to a tar. The rearrangement was achieved with less polymerization by steam distilling the carbinol through 28% sulfuric acid. The resultant crude cinnamaldehyde in two experiments was converted directly to the phenylhydrazone (35% over-all yield). In a third experiment the aldehyde was converted to α-bromocinnamaldehyde (21% over-all yield).

Experimental

Rearrangement of Phenylethynylcarbinol.—Phenylethynylcarbinol (5.4 g.) and 5 cc. of water were placed in a 25-cc. distilling flask fitted for steam distillation with the side arm extending nearly to the bottom of the 50-cc. flask of a Clark acetyl apparatus[7] containing 25 cc. of 28% sulfuric acid. The flasks were heated in oil-baths to 115°, a steam generator connected to the small flask, and steam distillation started adjusting the bath temperatures to maintain approximately constant volume in the flasks. A water-insoluble oil (3.1 g.) separated in the distillate and dissolved in 5 cc. of ethanol. A solution of 17.5 g. phenylhydrazine hydrochloride and 10.0 g. sodium acetate in 150 cc. of water then was added to the oil and the mixture warmed for fifteen minutes on a water-bath. After filtering, washing with water, ethanol and ether, and drying, 3.0 g. (33%) of crude cinnamalphenylhydrazone (m. p. 154–157°) was obtained. Two recrystallizations from ethanol raised the m. p. to 168–169° and a mixed m. p. with an authentic sample showed no depression. A second experiment yielded 1.2 g. (36%) of the crude phenylhydrazone (m. p., 161–165°) from 2.0 g. of the carbinol.

The crude cinnamaldehyde from a similar rearrangement of 6.2 g. of phenylethynylcarbinol was extracted from the distillate with ether, and upon removal of solvent the oil was taken up in 10 cc. of glacial acetic acid. A solution of 10.7 g. of bromine in 19.9 g. of acetic acid was added dropwise with stirring and cooling in an ice-bath until the bromine color remained for ten minutes (10.3 g. of the solution, corresponding to 3.0 g. cinnamaldehyde, was required.) Potassium carbonate (1.5 g.) was then added and the mixture allowed to stand overnight at room temperature. After refluxing thirty-five minutes, the mixture was cooled and poured into 30 cc. of water, whereupon an oil separated that partially crystallized upon shaking. The oil and crystals were removed and taken up in 10 cc. of warm ethanol. Upon cooling and seeding 2.1 g. (21%) of α-bromocinnamaldehyde, m. p., 71.5–72°, was obtained. Recrystallization from ethanol did not alter the m. p., and the mixed m. p. with a sample prepared following the directions of Allen and Edens[8] showed no depression.

---

[1] Rupe and Kambli, *Helv. Chim. Acta*, **9**, 672 (1926).
[2] Rupe and Keunzy, *Helv. Chim. Acta*, **14**, 708 (1931).
[3] Meyer and Schuster, *Ber.*, **55**, 819 (1922).
[4] Fischer and Lowenberg, *Ann.*, **475**, 183 (1929).
[5] Hurd and Christ, THIS JOURNAL, **59**, 118 (1937).
[6] Chanley, THIS JOURNAL, **70**, 244 (1948).
[7] Clark, *Ind. Eng. Chem., Anal. Ed.*, **8**, 487 (1936).
[8] Allen and Edens, "Organic Syntheses," **25**, 92 (1945).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF PORTLAND
PORTLAND 3, OREGON RECEIVED JUNE 1, 1948

Indium Orthovanadate[1]

BY W. O. MILLIGAN, HENRY H. RACHFORD, JR., AND L. MERTEN WATT

Forty-seven years ago Renz[2] prepared a gel which he designated as $In(VO_3)_3{\cdot}2H_2O$ by the addition of a sodium metavanadate solution to an indium chloride solution. The supposed constitution of the gel was based merely upon a chemical analysis, and there does not exist in the literature.

---

[1] Presented before the Texas Regional Meeting of the American Chemical Society held in Austin, Texas, December 7–8, 1945.
[2] Renz, *Ber.*, **34**, 2765 (1901).

any definite evidence concerning the constitution or even the existence of indium vanadates.

The purpose of this present investigation was to attempt to prepare a definite indium vanadate.

Experimental.—Seven samples in the system indium trioxide–vanadium pentoxide were prepared by wet and dry methods as outlined in the table. The samples were examined by standard X-ray diffraction methods, using Cr Kα X-radiation. The Kβ X-radiation was removed completely by a supplementary filter of vanadium pentoxide. The results of X-ray analysis are likewise summarized in the table.

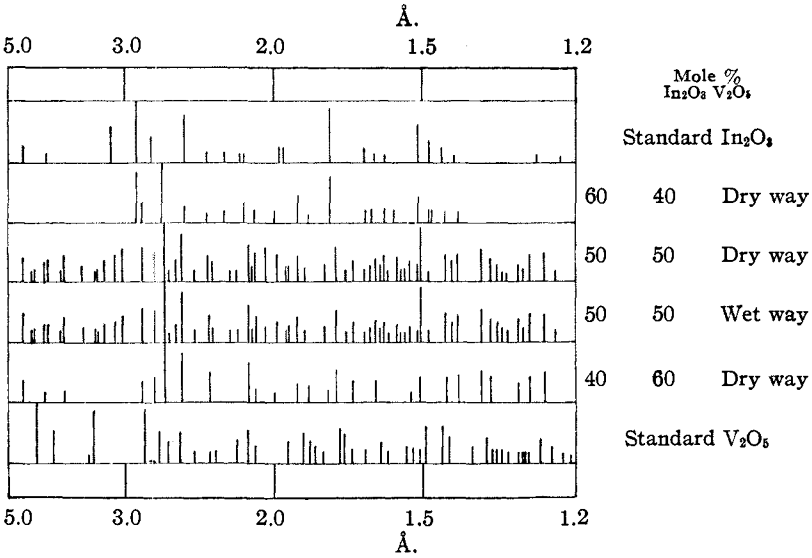

Fig. 1.—X-Ray diffraction patterns.

TABLE I

Sample	Method of preparation	Results of X-ray analysis
1	An equimolar amount of $InCl_3$ solution (0.1 *M*) was added rapidly to 100 ml. of saturated NH_4VO_3 solution at room temperature. The yellowish gel was washed in a centrifuge and dried in air	Amorphous to X-rays
2	An equimolar amount of $InCl_3$ solution (0.1 *M*) was added rapidly to 100 ml. of NH_4VO_3 solution (saturated at 90°). The gel was washed in a centrifuge, and dried at 120°	Amorphous to X-rays
3	Sample no. 1 heated for two hours at 850°	Pattern consists of numerous sharp lines distinct from those of In_2O_3 or V_2O_5
4	Sample no. 2 heated for two hours at 1000°	Pattern identical with no. 3
5	Equimolar quantities of dry $In(OH)_3$ and dry NH_4VO_3 were ground for two hours in a motor-driven agate mortar, and were heated for two hours at 850°	Pattern identical with nos. 3 and 4
6	Prepared as no. 5, except the amounts of dry powders were taken to give 40 mole % In_2O_3 and 60 mole % of V_2O_5	Pattern consists of all lines found in no. 5 plus some weak V_2O_5 lines
7	Prepared as no. 5, except the amounts of dry powders were taken to give 60 mole % of In_2O_3 and 40 mole % V_2O_5	Pattern consists of all lines found in no. 5 plus some weak In_2O_3 lines

Discussion.—It will be noted that both gels prepared by precipitation are amorphous to X-rays. There is no indication of the formation of a definite crystalline indium vanadate. It is not known whether these gels consist of an amorphous indium vanadate or of a mixture of amorphous indium oxide or hydroxide together with amorphous vanadium pentoxide.

Samples heated to temperatures of 850–1000° are sub-microscopically crystalline and yield a diffraction pattern consisting of numerous relatively sharp lines. This pattern is distinct from those of anhydrous In_2O_3 or V_2O_5, and is therefore assumed to be characteristic of a definite indium vanadate. Since samples containing excess of either component yield diffraction lines from the excess oxide, it is believed that the compound formed is indium orthovanadate, $InVO_4$. X-Ray diffraction patterns for $InVO_4$, In_2O_3 and V_2O_5 are given in chart form in Fig. 1. The data cannot be indexed in the cubic or tetragonal crystal systems. The numerical data of the observed interplanar spacings and visually estimated intensities have been tabulated and included in the card index file of the American Society for Testing Materials (ASTM).

DEPARTMENT OF CHEMISTRY
THE RICE INSTITUTE
HOUSTON, TEXAS

RECEIVED JUNE 23, 1948

Absorption Spectra of 4-(4-Diethylamino-1-methylbutylamino)-7-phenoxyquinoline and 4-(4-Diethylamino-1-methylbutylamino)-7-ethoxy-3-methylquinoline

BY FREDERICK C. NACHOD, EDGAR A. STECK AND GALEN W. EWING[1]

A comparison of the absorption spectra of 4-(4-diethylamino-1-methylbutylamino)-7-phenoxy-

---

[1] Present address: Department of Chemistry, Union College, Schenectady 8, N. Y.