distillation of large quantities of isosafrole dibromide,[9] the crude dibromide was dissolved in 260 g. of dry diethylene glycol containing 44 g. of potassium hydroxide, and the mixture was heated with stirring at 130° for five hours. Potassium bromide precipitated during the heating. The reaction mixture was poured into twice its volume of water, extracted twice with ether, the ether extract dried over anhydrous potassium carbonate, and the ether removed. In addition to the desired propyne IV, the residue contained some 3,4-methylenedioxypropiophenone; the product was best purified by extracting the red oil three times with *n*-pentane, in which IV was very soluble and the ketone was only slightly soluble. The yellow *n*-pentane solution was dried over potassium carbonate, the solvent removed, and the residual oil distilled *in vacuo*. The propyne was obtained as a colorless oil (16 g., 54%) b. p. 136–138° (14 mm.); it solidified on cooling, m. p. 40.5–42° (reported,[8] 42–43°). There was much residue in the distilling flask.

Two other procedures for purification of the crude material were investigated. The dry pentane solution (see above) was chromatographed on alumina; the propyne IV was not adsorbed, and was thus separated from a ketonic fraction which was adsorbed and which gave a highly fluorescent band under ultraviolet light. This procedure was unsatisfactory for large quantities because of the amount of alumina required.

Steam distillation, applied to the residue from the ether extract above, gave at first quite pure propyne, and the ketone appeared in the distillate as the distillation proceeded. The ketone obtained as a by-product in this reaction was shown to be 3,4-methylenedioxypropiophenone by preparation of the oxime, m. p. 103.5–104.5°.[10] The 2,4-dinitrophenylhydrazone was also prepared; m. p. 256–257° (uncor.) with decomposition.

Anal. Calcd. for $C_{16}H_{14}N_4O_6$: C, 53.63; H, 3.94. Found: C, 53.77; H, 3.85.

This ketone was also prepared from the propyne IV by the method of Foulds and Robinson,[8] and was found by its derivatives to be identical with the ketone obtained above as a by-product from the action of alkali on isosafrole dibromide.

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[9] Waterman and Priester, *Rec. trav. chim.*, **48**, 941 (1929); their observations have been duplicated by us.

[10] This oxime is reported by Wallach and Pond, *Ber.*, **28**, 2719 (1895), to melt at 104°.

DEPARTMENT OF CHEMISTRY
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RECEIVED MARCH 2, 1949

Solubility of Nitroaminoguanidine

BY WILLIAM MCBRIDE,[1] RONALD A. HENRY AND G. B. L. SMITH

The solubility of nitroaminoguanidine, $NH_2NHC(NH)NHNO_2$, in unbuffered aqueous solutions (*p*H 6.40 at 30°) has been determined in the temperature range 10 to 50° (Fig. 1) and can be expressed with an accuracy of two per cent. by the equation: log (solubility in g./100 g. of water) = $(-1916.7/T) + 5.9632$, calculated from the data by the method of least squares. In a 0.25 molal solution of sodium phosphate (*p*H 6.96 to 7.04 at 30°) the solubility is approximately six per cent. greater throughout the same range (Fig. 1) and can be expressed as: log (solubility in g./100 g. of water) = $(-1914.1/T) + 5.9801$.

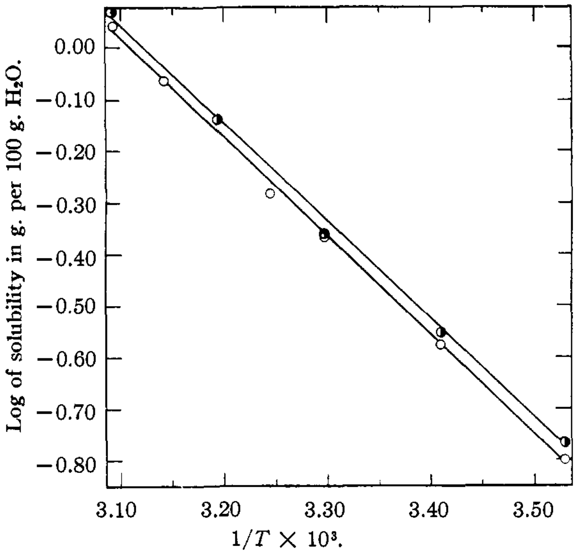

Fig. 1.—Solubility of nitroaminoguanidine in distilled water (○), and in a 0.25 molal solution of sodium phosphate (◑); *p*H 6.96–7.04 at 30°.

The effect of *p*H on the solubility of nitroaminoguanidine at 30° is shown in Fig. 2 and indicates the amphoteric nature of the compound; this is in agreement with the reported behavior of nitro-[2,3] and nitrosoguanidine.[3,4]

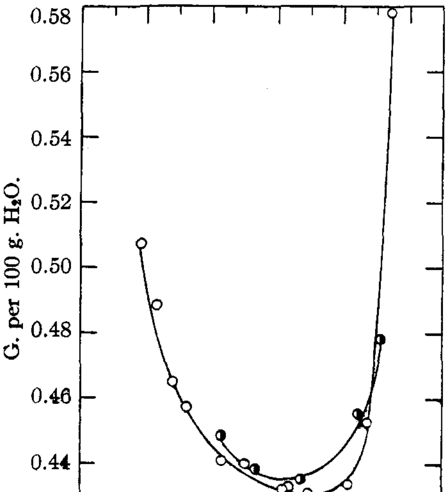

Fig. 2.—Solubility of nitroaminoguanidine at 30° as a function of *p*H: in water (○), and in 0.25 molal solution of sodium phosphate (◑).

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[1] Present address: Department of Chemistry, University of California at Los Angeles, Calif.

[2] Thiele, *Ann.*, **270**, 1 (1892).

[3] Hahn, Pribyl, Lieber, Caldwell and Smith, THIS JOURNAL, **66**, 1223 (1944).

[4] Thiele, *Ann.*, **273**, 133 (1893); Robertson, M.S. Thesis, Polytechnic Institute of Brooklyn, 1935; Sabetta, Himmelfarb and Smith, THIS JOURNAL, **57**, 2478 (1935).

Experimental

The nitroaminoguanidine was prepared by the method of Phillips and Williams,[5] and was recrystallized repeatedly from water to a purity of 99.9 ± 0.1% as determined by a Jamieson hydrazine nitrogen analysis.[6] The melting point is an unsatisfactory criterion for ascertaining the purity of this compound.

The solubility was determined in three types of aqueous systems: (1) distilled water, (2) distilled water in which the *p*H had been adjusted with a 0.1 N solution of hydrochloric acid or sodium hydroxide, and (3) 0.25 molal sodium phosphate buffer solutions made by mixing suitable ratios of mono-, di- or tri-sodium orthophosphate. About 1 g. of nitroaminoguanidine was dissolved in 100 ml. of such a solution in a glass-stoppered flask, the whole cooled to the desired temperature and kept at that temperature by a thermostat constant to ±0.1°. After two hours of agitation (longer might cause hydrolysis) samples of 5 to 25 g. were removed by pressure filtration through a fine-pored, sintered Pyrex glass filter stick into stoppered and tared iodine flasks. The cooled samples were weighed and then titrated with potassium iodate by the Jamieson[6] method. For a given set of conditions, the reproducibility of the solubility determination was about five parts per 1000. Suitable corrections have been applied to the determinations in the buffered solutions for the weight of dissolved phosphate, and the results expressed in grams per 100 g. of water.

The *p*H was measured at 30° on filtered samples of solution after temperature and solution equilibrium had been established.

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[5] Phillips and Williams, *ibid.*, **50**, 2465 (1928).

[6] Jamieson, *Am. J. Sci.*, **33**, 352-353 (1912); "Volumetric Iodate Methods," Chemical Catalog Co., Inc., New York, N. Y., 1926, p. 36. Also see Smith and Wheat, *Ind. Eng. Chem.*, *Anal. Ed.*, **11**, 200 (1939).

INORGANIC CHEMISTRY SECTION
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RECEIVED FEBRUARY 23, 1949

Acetic Propionic Anhydride

BY J. B. POLYA AND T. M. SPOTSWOOD

In the course of investigating acylating mechanisms by unsymmetrical acylating agents, acetic propionic anhydride was required. The only reference to this compound which we have been able to find is contained in a paper of Verkade[1] who has prepared it from propionyl chloride and potassium acetate and who has determined the hydrolytic constant. Verkade determined the molecular weight by saponification and concluded from this determination that his product was a pure compound. It is true that previous distillation of the product at a boiling point intermediate between those of acetic and propionic anhydrides made the presence of an exactly equimolecular mixture of acetic and propionic anhydrides very unlikely, but it was felt that a more rigorous proof of purity would be desirable.

Anhydrous sodium acetate (20 g.) was made into a paste with dry ether (20 cc.); propionyl chloride (20 g.) was added gradually while the mixture was cooled with water. On completing the addition the mixture was refluxed on a water-bath for two hours. More ether (20 cc.) was added, the mixture was filtered, the ether removed and the residue fractionated under reduced pressure. The first fraction boiling between 55 and 61° under 29 mm. pressure was discarded. The next fraction distilled between 61 and 67° at the same pressure. The residue consisted of an oil which did not boil below 160° (29 mm.). The second fraction was redistilled at 70–75° (40 mm.) with very little loss. This fraction boiled at 153.5° at 760 mm. without decomposition and was shown to be pure acetic propionic anhydride. The yield was 15 g. or 60%.

The boiling point at 40 mm. pressure is identical with the one reported by Verkade. The average boiling points at three pressures fit well on a Clausius-Clapeyron line. Assuming absence of association, the molecular weight was found to be 116.5 by saponification. At 17° the specific gravity was 1.0367 and the refractive index n_D 1.4020. The molecular refractivity from these data is 27.26 against 26.96 required by theory.

Acetic propionic anhydride (5.00 g.) and absolute ethanol (1.98 g.) was refluxed for forty-five minutes. The mixture was chilled and diluted with ice-water. The mixed esters were isolated by separating the supernatant layer of esters, extracting the residue with ether and then washing and drying the ethereal solution of the esters before removing the solvent. A portion of the mixed esters was saponified by normal alcoholic alkali and titrated with 0.1 N hydrochloric acid. In this manner the mixture was found to contain 64.4% ethyl acetate and 35.6% ethyl propionate. Previous experiments of a similar nature with N-acetylpropionamide gave 62–66% ethyl acetate and 34–38% ethyl propionate.[2] When the experiment was repeated with the same quantities using an equimolecular mixture of acetic and propionic anhydrides the ester mixture was found to contain 50.7% ethyl acetate and 49.3% ethyl propionate.

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[1] Verkade, *Rec. trav. chim.*, **35**, 299 (1916).

[2] Polya and Spotswood, *ibid.*, **67**, 927 (1948).

CHEMISTRY DEPARTMENT
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HOBART, AUSTRALIA
RECEIVED DECEMBER 27, 1948

The Preparation of 3-Iodoalizarin

BY MARGARET G. PRATT AND S. ARCHER

In the course of some biological studies, it became desirable to have at hand an alizarin derivative which was opaque to X-rays. Accordingly, we investigated the preparation of 3-iodoalizarin, a substance which seemed to fulfill the requirements.

The compound has been prepared previously by Perkin and Story[1] who iodinated alizarin-1-methyl ether (1-methoxy-2-hydroxyanthraquinone) and then demethylated the product. Unfortunately the starting material is difficultly accessible and the synthesis does not appear to be adaptable to larger scale preparations.

The procedure we employed is outlined below. 3-Nitroalizarin[2] was methylated previously by Perkin[3] who employed the dipotassium salt and a large excess of sodium carbonate and methyl sulfate. We were able to duplicate their experiment only once and found subsequently that a minor variant in detail, namely, doubling the recommended amount of sodium carbonate, ensured the reproducibility of their preparation. The conversion of the nitro ether, I, to the amine, II and the iodo ether, III, was carried out according to more or less established procedures. De-

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[1] Perkin and Story, *J. Chem. Soc.*, 2620 (1931).

[2] Schunk and Roemer, *Ber.*, **12**, 584 (1879).

[3] Perkin and Story, *J. Chem. Soc.*, 1416 (1929).