Benzalacetone reacted with morpholine and sulfur under the same conditions to form γ-phenylvinylthioacetomorpholide (II) in 35% yield. Ozonolysis of (II) followed by reductive cleavage yielded benzaldehyde which was identified by its dimethone derivative. Hydrolysis of (II) with alcoholic potassium hydroxide yielded only unchanged starting material, but long refluxing with hydrochloric acid and acetic acid yielded a product (III) melting at 112–114°, soluble in base and containing neither nitrogen halogen nor sulfur. Analyses of (III) approximated an empirical formula of $C_7H_7O_2$, but a neutral equivalent of 189–195 and a mixed melting point indicated that the product was not benzoic acid.

Experimental[5]

γ-Phenylethynylthioacetomorpholide.—Acetylphenylacetylene (29 g., 0.2 mole), 26 g. (0.3 mole) of morpholine and 9.6 g. of sulfur were heated gently for one hour and then refluxed vigorously for three hours more. The reaction mixture was cooled, taken up in 200 cc. of benzene, washed with dilute hydrochloric acid and finally with water. The benzene solution was dried, the benzene removed and the residue recrystallized first from aqueous alcohol and finally from Skellysolve A. The thioacetomorpholide (I) crystallized in pale yellow amorphous knobs, m. p. 79-80°; yield 25 g. (51%).

Anal. Calcd. for $C_{14}H_{15}ONS$: C, 68.53, H, 6.16. Found: C, 68.34; H, 6.52.

Ozonolysis of 0.1 g. of (I) in carbon tetrachloride at 0° followed by oxidative cleavage yielded benzoic acid, melting point and mixed melting point, 121°.

When 2 g. of (I) was refluxed for ten hours with 20% alcoholic potassium hydroxide or with a solution of 2 cc. of concentrated hydrochloric acid in 15 cc. of glacial acetic acid, only starting material was recovered.

γ-Phenylvinylthioacetomorpholide (II).—Benzalacetone (30 g., 0.2 mole), 26 g. (0.3 mole) of morpholine and 9.6 g. (0.3 mole) of sulfur were heated gently for one hour and then refluxed vigorously for four hours. The product was worked up as described above except that the tarry residue was recrystallized from aqueous alcohol and finally treated with boneblack to remove the color. The thioacetomorpholide (II) crystallized in white plates, m. p. 133-134°; yield, 17 g. (35%).

Anal. Calcd. for $C_{14}H_{17}ONS$: C, 67.98; H, 6.93; N, 5.67. Found: C, 67.93; H, 6.57; N, 5.85.

The thioacetomorpholide (II) (80 mg.) dissolved in ethyl bromide was ozonized at 0°. The solvent was removed and the solid ozonide was decomposed reductively in the usual manner. The benzaldehyde was isolated as the dimethone derivative, melting point and mixed melting point 194-195°.

Hydrolysis of (II).—The thioacetomorpholide (II) (2 g.), 2 cc. of hydrochloric acid and 15 cc. of acetic acid were refluxed vigorously for ten hours. The reaction mixture was poured into water and after standing overnight the solution and suspended solid were extracted with ether. The ether extract was dried, the ether removed and the gummy residue was sublimed. A white solid (III) was obtained which melted at 112-114°[6] and contained no nitrogen or sulfur. The product was soluble in base but the melting point of the recovered acid was unchanged. A mixture of benzoic acid and (III) melted at 100-105°.

Anal. Calcd. for γ-phenylvinylacetic acid, $C_{10}H_{10}O_2$: C, 74.04; H, 6.21; neut. equiv., 162. Found: C, 67.10; H, 5.95; neut. equiv., 189, 195.

When (II) was refluxed with 20% alcoholic potassium hydroxide for ten hours, only unchanged starting material was isolated.

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RECEIVED MAY 20, 1949

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[5] The semimicro carbon-hydrogen analyses were done by R. A. Carpenter.

[6] The recorded melting point of γ-phenylvinylacetic acid is 86°. Fittig and Jayne, *Ann.*, **216**, 98 (1883).

N-(*p*-Chlorophenyl)-diamidophosphoric Acid

BY KURT RORIG

A compound considered to be N-(*p*-chlorophenyl)-amidophosphoric acid, *p*-$ClC_6H_4NHPO(OH)_2$, on the basis of an elemental analysis for carbon and hydrogen was first prepared by Otto[1] in 1895. Recently it has been prepared by Otto's method for use as an enzymatic substrate in histochemical experiments.[2]

This compound was also prepared according to Otto in our laboratory and was found to have the melting point reported by him. A complete elemental analysis, however, showed it to be N-(*p*-chlorophenyl)-diamidophosphoric acid, *p*-$ClC_6H_4NHPO(OH)(NH_2)$, rather than the monoamidophosphoric acid postulated by Otto. In accordance with the diamidophosphoric acid structure, the titration curve of our compound showed only the one break characteristic of a monobasic acid. A mixed melting point determination has shown that Gomori's compound[2] is the same as ours. However, our N-(*p*-chlorophenyl)-diamidophosphoric acid, melting at 156–157°, is insoluble both in hot water and in hot ethanol; whereas Otto reported that his compound, melting at 155°, was soluble in these solvents. Since Otto has also reported the existence of a di-silver salt of his compound, it is prudent to say only that by following his somewhat incomplete instructions as closely as possible, N-(*p*-chlorophenyl)-diamidophosphoric acid was obtained by Gomori and ourselves.

Furthermore, the formation of the diamidophosphoric acid is in harmony with the experience of Caven,[3] who found that anilidophosphoryl-dichloride, when dissolved in aqueous ammonia, formed N-phenyl-diamidophosphoric acid rather than the monoamidophosphoric acid as surmised by Michaelis and Schulze.[4]

Experimental

A mixture of 163.5 g. (1 mole) of *p*-chloroaniline hydrochloride and 307 g. (2 moles) of phosphorus oxychloride was refluxed for two and one-half hours. The cooled, solidified reaction mixture was filtered and washed with petroleum ether (b. p. 60–71°) to give 202 g. of crude *p*-chloroanilidophosphoryl-dichloride, *p*-$ClC_6H_4NHPOCl_2$, melting at 97–104°. A small sample melted at 105–107° when recrystallized from benzene.

Thirty grams of crude *p*-chloroanilidophosphoryl dichloride was added slowly to 60 ml. of aqueous ammonium hydroxide (28%) while keeping the temperature below 10°. The turbid solution was immediately filtered and acidified with a slight excess of hydrochloric acid to precipitate the

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[1] Otto, *Ber.*, **28**, 617 (1895).

[2] Gomori, *Proc. Soc. Exp. Biol. Med.*, **69**, 407 (1948); *ibid.*, **70**, 7 (1949).

[3] Caven, *J. Chem. Soc.*, **81**, 1367 (1902).

[4] Michaelis and Schulze, *Ber.*, **26**, 2939 (1893).

gelatinous N-(*p*-chlorophenyl)-diamidophosphoric acid. This crude product when filtered, washed thoroughly with water and dried, weighed 19.5 g. and melted 143–148°. The crude N-(*p*-chlorophenyl)-diamidophosphoric acid was purified by washing first with boiling water, then with hot ethanol and finally with ether. It then melted at 156–157° and had a neutral equivalent of 203 (calcd. 206.5).

Anal. Calcd. for $C_6H_8ClN_2O_2P$: C, 34.88; H, 3.90; Cl, 17.17; N, 13.56; P, 15.00. Found: C, 34.94; H, 3.77; Cl, 17.20; N, 13.26 (Kjeldahl), 13.29 (Dumas); P, 14.4.

The melting point of the mixture of Gomori's compound (m. p. 153–154°)[5] with ours (m. p. 156–157°) was 154–155.5°.

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[5] We wish to thank Dr. Gomori for providing this sample.

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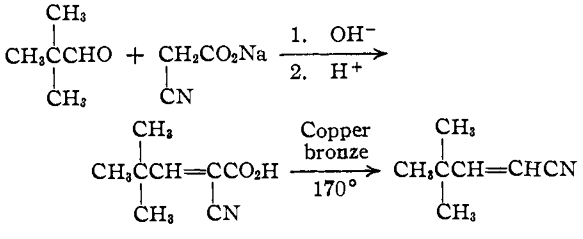
RECEIVED MAY 20, 1949

The Preparation of Some β-Alkylated Acrylonitriles

BY ROBERT M. ROSS[1] AND MARY LOUISE BURNETT

Certain nitriles; namely, β-*t*-butylacrylonitrile, β-isopropylacrylonitrile and β-ethylacrylonitrile were needed for studies which were in progress in this Laboratory. No method for the synthesis of β-*t*-butylacrylonitrile could be found in the literature and, although preparative methods exist for β-isopropylacrylonitrile and β-ethylacrylonitrile,[2] they appeared unnecessarily arduous. Accordingly, new routes for the syntheses of the desired nitriles have been investigated.

β-*t*-Butylacrylonitrile has been prepared by the condensation of pivalaldehyde with sodium cyanoacetate[3] in an aqueous, alkaline medium and subsequent decarboxylation of the cyano acid thus obtained.

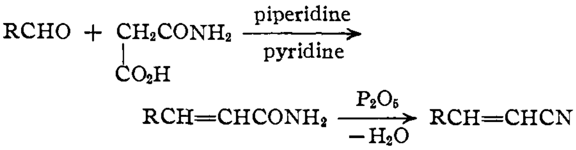


$$\mathrm{CH_3\overset{CH_3}{\underset{CH_3}{C}}CHO} + \underset{CN}{\mathrm{CH_2CO_2Na}} \xrightarrow[2.\ H^+]{1.\ OH^-}$$

$$\mathrm{CH_3\overset{CH_3}{\underset{CH_3}{C}}CH{=}\underset{CN}{C}CO_2H} \xrightarrow[170^\circ]{\text{Copper bronze}} \mathrm{CH_3\overset{CH_3}{\underset{CH_3}{C}}CH{=}CHCN}$$

The over-all yield for the method is about 45%.

Galat[4] reported a novel synthesis of α,β-unsaturated amides which involved the condensation of aromatic aldehydes with malonmonoamide. We have extended the use of malonmonoamide to include condensations with some aliphatic aldehydes. β-Isopropylacrylamide and β-ethylacrylamide were prepared in this manner. The amides were then dehydrated by the usual method using phosphorus pentoxide.



$$\mathrm{RCHO} + \underset{CO_2H}{\mathrm{CH_2CONH_2}} \xrightarrow[\text{pyridine}]{\text{piperidine}}$$

$$\mathrm{RCH{=}CHCONH_2} \xrightarrow[-H_2O]{P_2O_5} \mathrm{RCH{=}CHCN}$$

This synthesis affords over-all yields of about 56 and 20% for the β-isopropyl- and β-ethylacrylonitriles, respectively. A previously reported[2] method for the preparation of these nitriles consisted of a relatively tedious four-step synthesis and furnished β-isopropylacrylonitrile in about 18% yield; no over-all yield was reported for β-ethylacrylonitrile. Thus, the use of malonmonoamide eliminates two reaction steps and affords significantly greater yields at least in the preparation of β-isopropylacrylonitrile.

Experimental

Pivalaldehyde.—Trimethylpyruvic acid[5] was decarboxylated in the presence of diphenylamine to yield pivalaldehyde according to the directions of Trister and Hibbert.[6]

Malonmonoamide.—Galat's[4] procedure for the synthesis was employed.

α-Cyano-β-*t*-butylacrylic Acid.—A mixture of 126 ml. of 2.65 *M* sodium cyanoacetate solution,[7] 1.63 g. of sodium hydroxide pellets and 85 ml. of water were placed in a 500-ml., three-necked, round-bottomed flask equipped with a rubber-sealed Hershberg stirrer, condenser and thermometer. To the contents of the flask was added 19.0 g. (0.24 mole) of pivalaldehyde and vigorous stirring was commenced. The contents of the flask were heated to 50° for fifteen minutes by a warm water-bath. At the end of this time, the bath was removed and stirring was continued for two hours. Then an additional 40 ml. of 2.65 *M* sodium cyanoacetate solution and 0.51 g. of sodium hydroxide pellets were added to the reaction mixture. The contents of the flask were reheated to 50° for fifteen minutes and stirring was continued for three hours longer. At the end of this time, the solution was made neutral to litmus by the careful addition of concentrated hydrochloric acid. A 20-ml. excess of hydrochloric acid was added to the neutral solution. The brown oil which formed was induced to crystallize by scratching the flask sides with a glass rod. After thorough chilling at 0°, the tan-colored crystals of α-cyano-β-*t*-butylacrylic acid were removed by filtration, suction dried on the filter funnel, and washed with 30 ml. of cold benzene. A total of 26 g. (71%) of crude α-cyano-β-*t*-butylacrylic acid was isolated, m. p.[8] 115–119° (dec.). Recrystallization was effected from about 150 ml. of dilute ethanol (10%) with Norit. Long, white needles were obtained, m. p. 123.5–125° (slight dec.).

Anal.[9] Calcd. for $C_8H_{11}O_2N$: C, 62.72; H, 7.24; N, 9.15; neut. equiv., 153. Found: C, 62.70; H, 7.30; N, 8.99; neut. equiv., 157.

β-*t*-Butylacrylonitrile.—In a 50-ml., round-bottomed flask, equipped with mechanical stirrer and condenser, were placed 6.5 g. (0.042 mole) of α-cyano-β-*t*-butylacrylic acid and 1.5 g. of fine copper–bronze powder. The contents of the flask were heated by an electrically controlled oil-bath. The temperature of the oil-bath was raised rapidly to 170°. When the cyano acid melted (about 125°), stirring was started and the evolution of carbon dioxide was noted by leading an exit tube from the condenser top into a test-tube of water. The evolution of carbon dioxide became rapid when the bath temperature was 140°, and at 160°

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[1] Preliminary investigations of this work were carried out by one of us (R. M. R.) as the du Pont postdoctoral fellow.

[2] von Auwers, *Ann.*, **432**, 46 (1923).

[3] A similar method was employed in the preparation of α-cyano-β-phenylpyruvic acid; see Lapworth and Baker, "Organic Syntheses," Coll. Vol. I, p. 181.

[4] Galat, THIS JOURNAL, **70**, 2596 (1948).

[5] Richard, *Ann. chim. phys.*, [8] **21**, 360 (1910).

[6] Trister and Hibbert, *Can. J. Research*, **14B**, 415 (1936).

[7] Lapworth and Baker, "Organic Syntheses," Coll. Vol. I, p. 181.

[8] All melting points reported herein are uncorrected.

[9] The analyses reported were done by the Clark Microanalytical Laboratories, Urbana, Illinois.