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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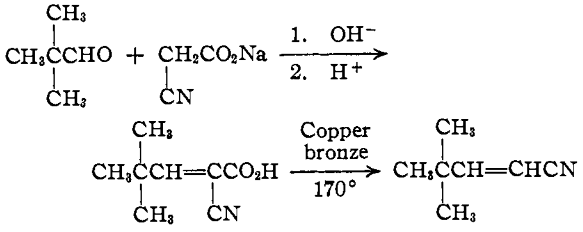
The Preparation of Some β-Alkylated Acrylonitriles

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.

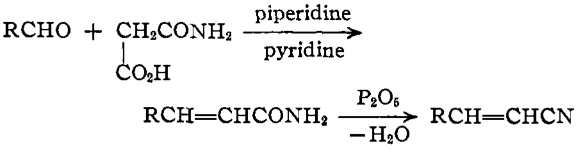


$$\mathrm{CH_3}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{CHO} + \underset{\mathrm{CN}}{\mathrm{CH_2}}\mathrm{CO_2Na} \xrightarrow[\text{2. H}^+]{\text{1. OH}^-}$$

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

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.



$$\mathrm{RCHO} + \underset{\mathrm{CO_2H}}{\mathrm{CH_2}}\mathrm{CONH_2} \xrightarrow[\text{pyridine}]{\text{piperidine}}$$

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

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.

it was vigorous. After twenty-five minutes of heating at 170°, carbon dioxide was no longer evolved. Heating was stopped and the melt was allowed to cool. The copper-bronze powder was removed by filtration with the aid of a small amount of ether. The powder was washed thoroughly with 25 ml. of ether which was combined with the filtrate. Ether was removed by distillation, and the residue was distilled under reduced pressure. A colorless and pungent smelling liquid, boiling between 59 and 60° (28 mm.) was obtained; $n^{20}\text{D}$ 1.4344. The yield was 3.2 g. (70%).

Anal.[9] Calcd. for $C_7H_{11}N$: C, 77.01; H, 10.16. Found: C, 77.16; H, 10.16.

β-Isopropylacrylamide.—In a 100-ml., round-bottomed flask were placed 10.8 g. (0.15 mole) of freshly distilled isobutyraldehyde, 30.9 g. (0.30 mole) of malonmonoamide, 25 ml. of dry pyridine and eight drops of dry piperidine. The mixture was heated under reflux (oil-bath temperature was 82°) for twenty-four hours. At the outset of the heating, there was a vigorous evolution of carbon dioxide, which gradually subsided over the twenty-four-hour period. At the end of this time, the mixture was concentrated to dryness under reduced pressure. The residue was diluted with 10 ml. of water and extracted with 250 ml. of ether in five 50-ml. portions. The ether extract was dried over anhydrous magnesium sulfate. Ether was removed by distillation whereupon the residue solidified. The crude, nearly white β-isopropylacrylamide was dried under a reduced pressure of less than 1 mm. overnight. The yield was 11.9 g. (70%), m. p. 79–84°. Recrystallization from 15 ml. of hot benzene gave 9.0 g. of white crystals which melted between 83 and 86° (lit.[2] 82–86°).

β-Isopropylacrylonitrile.—A mixture of 4.4 g. (0.039 mole) of β-isopropylacrylamide and 6.5 g. of phosphorus pentoxide was placed in a 100-ml., round-bottomed flask. The contents were mixed thoroughly. The flask was equipped with a small take-off head for downward distillation and the contents were heated gradually by an oil-bath. The temperature of the bath was brought to and maintained at 200°. At the end of thirty minutes the system was placed under a reduced pressure of about 50 mm. The distillate was collected in a tube immersed in a Dry Ice–acetone-bath. Heating was continued for about two hours and during this time the pressure was lowered gradually to 15 mm. The black residue frothed considerably during this period. At the end of this time, no further distillation took place and heating was stopped. A total of 3.0 g. of colorless β-isopropylacrylonitrile was obtained; $n^{20}\text{D}$ 1.4316. Redistillation yielded a product which possessed the following physical constants: $n^{20}\text{D}$ 1.4329, b. p. 68° (34 mm.). Reported[10] values for the *trans* compound are: $n^{20}\text{D}$ 1.4342, b. p. 48.5° (13.5 mm.).

β-Ethylacrylamide.—Essentially the same conditions were employed for the preparation of β-ethylacrylamide as those described for β-isopropylacrylamide. Crude β-isopropylacrylamide was isolated in the amount of 7.2 g. from 8.7 g. of freshly distilled propionaldehyde and 30.9 g. of malonmonoamide. Subsequent recrystallization from acetone afforded 3.4 g. of glistening, white needles, m. p. 148–148.5° (lit.[2] 148°).

β-Ethylacrylonitrile.—β-Ethylacrylamide was dehydrated with phosphorus pentoxide under essentially the conditions described for the preparation of β-isopropylacrylonitrile. A mixture of 6.28 g. (0.06 mole) of β-ethylacrylamide and 9.2 g. of phosphorus pentoxide yielded 2.3 g. (45%) of colorless β-ethylacrylonitrile, b. p. 72° (72 mm.), $n^{20}\text{D}$ 1.4301 (lit.,[11] b. p. 73° (72 mm.), $n^{20}\text{D}$ 1.4298 (for the *trans* compound)).

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Equilibria of the Boric Acid–Mannitol Complexes

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The recent publication by Deutsch and Osoling[1] on the stoichiometry and equilibria of boric acid–mannitol complexes prompts us to report some related results obtained in these laboratories. We have focused our attention on determining the equilibrium constant for the reaction

$$HB + 2M \rightleftharpoons BM_2^- + H^+$$

In determining this constant, we have consciously selected concentrations of both boric acid and mannitol which would permit us to make the simplifying assumption that the concentrations of both B^- and BM^- are negligible in comparison with the concentrations of both H^+ and BM_2^-. For the equilibrium constant, we may write

$$K = \frac{[H^+][BM_2^-]}{[HB][M]^2} \cong \frac{[H^+]^2}{[HB_0 - H^+][M_0 - 2H^+]^2}$$

and K can be calculated from a single *p*H measurement. The justification for this assumption will be discussed later.

The reagents were C.P. boric acid and mannitol and freshly boiled distilled water. All solutions were thermostatted at 25°, and the ionic strength was kept at 0.10–0.12 *M* by addition of C.P. potassium chloride. The *p*H's were measured with a Beckman *p*H meter. The results are summarized in Table I.

TABLE I

CALCULATED VALUES OF *K*

[HB]	[M]	[M]/[HB]	[KCl]	*p*H	$K \times 10^4$
0.0141	0.0534	3.78	0.117	4.20	1.01
.0166	.0985	5.94	.104	3.88	1.09
.0141	.0865	6.16	.117	3.99	0.955
.00532	.0370	6.95	.104	4.56	1.05
.00350	.0257	7.30	.114	4.81	1.05
.00350	.0292	8.30	.114	4.79	0.892
.00851	.0737	8.70	.104	4.17	1.00
.00350	.0374	10.7	.114	4.66	0.990

The average of these values is 1.00×10^{-4} and the maximum deviation from this average value is less than 11%. This agreement is as good as can be expected, since the uncertainty in the *p*H measurement is 0.02 unit, and a change of 0.02 in *p*H will change *K* by as much as 11%.

To check our accuracy, we determined the dissociation constant of boric acid in 0.104 *M* potassium chloride at 25.0°. The determined values ranged from 6.77×10^{-10} to 8.24×10^{-10}, with the average value being 7.40×10^{-10}. Again, all of the deviations from the average value can be accounted for by an uncertainty of 0.02 unit in the *p*H measurement. The accepted value for the dissociation constant in pure water is 6.4×10^{-10}, and a higher value is to be expected in our medium of higher ionic strength.[2]

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(10) Bruylants, *Bull. soc. chim. Belg.*, **41**, 309 (1932); *C. A.*, **27**, 267 (1933).

(11) Bruylants and Jmoudsky, *Bull. sci. acad. roy. Belg.*, [5] **17**, 1161 (1931); *C. A.*, **26**, 3232 (1932).

(1) Deutsch and Osoling, THIS JOURNAL, **71**, 1637 (1949).

(2) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1940, p. 89.