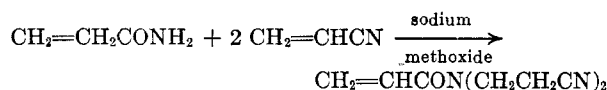


***N,N*-Bis(2-cyanoethyl)acrylamide**WALTER HARRY SCHULLER¹ AND DAVID CHESTER GUTH²*Received November 22, 1957*

The preparation of the new and interesting vinyl monomer, *N,N*-bis(2-cyanoethyl)acrylamide has been accomplished by the cyanoethylation of acrylamide.



This reaction was found to proceed smoothly, with a readily controlled evolution of heat, when carried out on a continuous basis at 45° with a reaction period (residence time) of 20 min. Excess acrylonitrile was employed as the solvent and a solution of sodium methoxide in methanol as the catalyst. The reactor effluent was run into a dilute aqueous solution of acetic acid with sufficient acetic acid always present to keep the mixture at pH 4-4.5. This treatment effectively quenched side reactions (as well as cyanoethylation) and minimized hydrolysis of the desired product.

Under the conditions described above, the competitive reactions expected were held in check, namely, the addition of methanol to acrylonitrile, and the base-catalyzed polymerization of acrylonitrile, acrylamide, and *N,N*-bis(2-cyanoethyl)acrylamide itself. The yield of *N,N*-bis(2-cyanoethyl)acrylamide could very likely be increased over that reported herein (54% based on acrylamide) as no effort to obtain a maximum yield was made.

The homopolymerization of *N,N*-bis(2-cyanoethyl)acrylamide and the copolymerization of this monomer with acrylamide and acrylonitrile were found to proceed readily in the presence of free-radical initiators.

N,N-Bis(2-cyanoethyl)acrylamide has been found effective as a plasticizer for polyacrylonitrile.³ This new vinyl compound may be useful as a comonomer in fields such as synthetic fibers. The presence of four functional groupings in one molecule should also make this compound attractive as a chemical intermediate.

EXPERIMENTAL⁴

Acrylamide was obtained from the New Product Development Department, American Cyanamid Co.

Acrylonitrile. The commercial product, obtained from American Cyanamid Co., was washed with dilute phosphoric

(1) Present address: Elkin Chemical Co., Inc., South Miami, Fla.

(2) Present address: R. T. Vanderbilt Co., Norwalk, Conn.

(3) D. C. Guth and E. J. Kerle, U. S. Patent 2,798,059 (1957).

(4) All melting points and boiling points corrected.

acid and fractionated through an efficient column, the middle cut being retained. The fraction contained 0.57% water. For storage purposes, 10 p.p.m. of *tert*-butyl catechol was added. Immediately before use, the stabilized acrylonitrile was passed through a column of activated alumina to remove both the inhibitor and the water present.

Sodium methoxide in methanol. This solution was prepared by dissolving the required amount of sodium metal in methanol.

Preparation of N,N-bis(2-cyanoethyl)acrylamide via a continuous process. The reactor consisted of a 700-ml. glass vessel 4½ in. in diameter, 7 in. high, having a dome cover, and provided 4 in. from the bottom with an overflow spout having an inside diameter of ¾ in. The dome cover was equipped with a stirrer, thermometer, monomer and catalyst feed lines, and a reflux condenser. The reactor was immersed to the overflow spout in a large, constant-temperature bath filled with glycerin. The overflow spout extended horizontally over the side of the constant-temperature bath, at which point the receiving vessel was located. The monomer solution was metered into the reactor by a gear pump. The catalyst-feeding device was a glass, piston-displacement feeder, operated by a clock motor. Both the monomer and the catalyst solutions were delivered at the bottom of the reactor by means of nitrogen pressure.

The monomer solution consisted of a mixture of 15 parts acrylamide and 85 parts acrylonitrile by weight. This represented a 7.55/1 molar ratio of acrylonitrile to acrylamide. The catalyst solution consisted of a 0.5*N* solution of sodium methoxide in methanol. The run was started by simultaneously introducing the monomer solution at a rate of 2180 ml./hr., and the catalyst solution, at a rate of 73 ml./hr. into the empty reactor, with the bath temperature at 45°. (Caution! Violent or explosive polymerization might occur should the temperature be allowed to rise far above 45°.) The temperature of the reaction was maintained at 45° throughout the run. One hundred seventy min. after the start of the run, steady state conditions were considered to have been obtained and the steady state product (SSP) was then collected for a total of 70 min. The SSP was collected in 32-oz. bottles, each of which contained 100 ml. of 0.33*N* acetic acid. The acid mixture was stirred during the collection of product. The pH of the acid SSP mixtures was 4-4.5 throughout. The effluent from the first 170 min. was not retained, although it undoubtedly contained a considerable quantity of *N,N*-bis(2-cyanoethyl)acrylamide.

The SSP from all of the 32-oz. bottles was combined, the organic layer washed twice with 500-ml. portions of 0.1*N* hydrochloric acid, and then washed with four 400-ml. portions of water. The washed acrylonitrile solution of the desired product was dried with sodium sulfate. The drying agent was removed by filtration and the filtrate was concentrated under reduced pressure. An aliquot was worked up and the yield of *N,N*-bis(2-cyanoethyl)acrylamide determined to be 40% based on acrylamide used. The work-up of the aliquot involved dissolution of the aliquot in acetone and precipitation, by the addition of methanol, of a yellow solid. This solid was identified as a polymer containing nitrile and amide groups. The yellow solid was removed by filtration and a small quantity of ethyl ether was added. Poly[*N,N*-bis(2-cyanoethyl)acrylamide] precipitated and was removed by filtration. Finally, an excess of ethyl ether was added to the filtrate and *N,N*-bis(2-cyanoethyl)acrylamide was obtained as a pale yellow, waxy precipitate. This was filtered, dried under reduced pressure over calcium chloride, and weighed.

The combined acetic acid layers, hydrochloric acid washings, and water rinses were extracted repeatedly with acrylonitrile, the combined extracts dried with sodium sulfate, filtered, and stripped under reduced pressure. The residue was treated with an excess of ethyl ether and the resulting white, waxy precipitate of *N,N*-bis(2-cyanoethyl)acrylamide collected by filtration, dried under reduced pressure over calcium chloride, and weighed. The yield obtained from

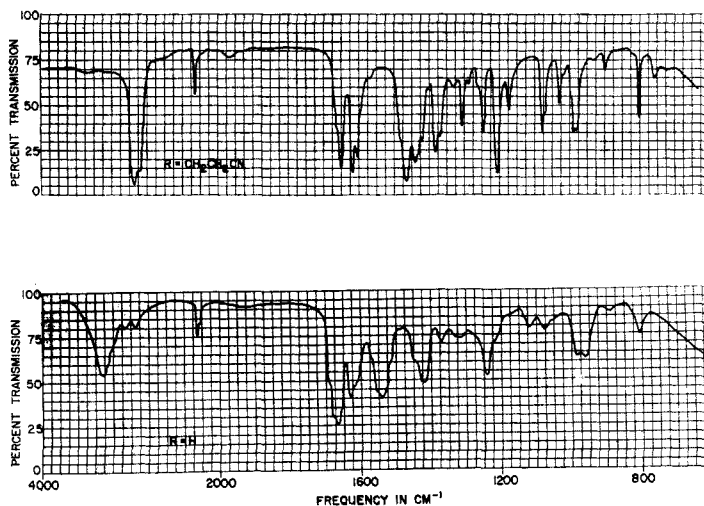


Fig. 1. Infrared spectra of cyanoethylated acrylamides, $\text{CH}_2=\text{CHCON}-(\text{R})\text{CH}_2\text{CH}_2\text{CN}$

this fraction was 14.5% based on acrylamide. The total yield was therefore 54.5% based on acrylamide charged to the reaction vessel during the period when SSP was being collected.

A portion of the crude monomer was recrystallized from an acrylonitrile-ethyl ether mixture to the constant m.p. 66.5° .

Anal. Calcd. for $\text{C}_9\text{H}_{11}\text{N}_3\text{O}$: C, 61.0; H, 6.22; N, 23.7. Found: C, 60.9; H, 6.30; N, 23.8.

An infrared absorption curve on the pure material confirmed the structure as being that of *N,N*-bis(2-cyanoethyl)acrylamide. (Fig. 1, R = $\text{CH}_2\text{CH}_2\text{CN}$.) This monomer was found to be soluble in acetonitrile, acrylonitrile, and hot benzene while insoluble in ethyl ether and cold benzene.

Homopolymerization of N,N-bis(2-cyanoethyl)acrylamide.

(a) *Benzoyl peroxide initiator.* To a solution of 1 g. of *N,N*-bis(2-cyanoethyl)acrylamide in 9 g. of benzene was added 0.04 g. of benzoyl peroxide. The clear solution was refluxed for 2 hr. The white insoluble polymer which precipitated from solution during the heating period was filtered, washed thoroughly with fresh benzene, and dried under reduced pressure. The yield of poly-*[N,N*-bis(2-cyanoethyl)acrylamide] was 0.64 g. (64%). This product was insoluble in methanol, water, and benzene. It was soluble in acetonitrile. The polymer softened at $143\text{--}144^\circ$ on a Fisher-Johns melting point apparatus. The specific viscosity of the polymer in dimethyl formamide was 0.30 at 30° (1 g./100 ml.).

(b) *α,α' -Azobisisobutyronitrile initiator.* A 50-ml. round-bottom flask equipped with a reflux condenser was charged with a solution of 2 g. of *N,N*-bis(2-cyanoethyl)acrylamide in 8 g. of benzene and the flask purged with nitrogen for 0.5 hr. To this solution was added 0.04 g. of α,α' -azobisisobutyronitrile and the clear solution was refluxed on a steam bath under nitrogen for 5 hr. The insoluble polymer which formed during this time was collected by filtration, triturated with fresh benzene and air-dried. The yield of poly-*[N,N*-bis(2-cyanoethyl)acrylamide] was 1.4 g. (70%). For purification, the crude product was dissolved in acetonitrile, the solution was filtered by gravity, and the polymer was precipitated by the addition of ethyl ether. This process was carried out twice. The amount of purified polymer recovered was 1 g. An infrared absorption curve on the purified product indicated that little, if any, hydrolysis of the polymer had occurred during polymerization and purification. The molecular weight was found to be approximately 10,000 by microisopiestic measurement. The polymer softened at $163\text{--}164^\circ$ on a Fisher-Johns melting point apparatus. The polymer was insoluble in water, methanol, ethyl ether, and benzene but soluble in acetonitrile.

Anal. Calcd. for $\text{C}_9\text{H}_{11}\text{N}_3\text{O}$: N, 23.7. Found: N (Kjeldahl), 22.6, 22.4.

Copolymerization of N,N-bis(2-cyanoethyl)acrylamide with acrylamide. To a 100-ml. round-bottom flask equipped with reflux condenser were added 2 g. of *N,N*-bis(2-cyanoethyl)acrylamide, 2 g. of acrylamide, and 36 g. of benzene. The solution was purged with nitrogen for 0.5 hr. and 0.08 g. benzoyl peroxide added.

The solution was refluxed under a nitrogen atmosphere for 5.5 hr. The copolymer which precipitated from solution during the reflux period was collected by filtration, triturated with fresh benzene, and air-dried. It weighed 3.6 g. (90%). For purification purposes, it was dissolved in formamide, filtered through a sintered glass funnel and precipitated by pouring into a large excess of ethanol. The precipitate was collected by filtration, washed thoroughly with ethanol, and dried. The purified polymer softened at $197\text{--}199^\circ$ when heated on a Fisher-Johns melting point apparatus. The Kjeldahl nitrogen content was found to be 20.8%. This would indicate the copolymer to contain about 50% acrylamide on a weight basis. This estimate was confirmed by an analysis of infrared absorption curves.

(b) *Acrylonitrile as a comonomer.* To a 50-ml. round-bottom flask were added 1 g. of *N,N*-bis(2-cyanoethyl)acrylamide, 3 g. of acrylonitrile, and 36 g. of benzene. The mixture was purged with nitrogen under a reflux condenser for 0.5 hr. The solution was then heated under reflux for 5.5 hr. The copolymer which precipitated during the polymerization was filtered, triturated with fresh benzene, and dried. It weighed 2.0 g. (50%). The crude copolymer was dissolved in a small amount of a 1/1 mixture (by volume) of dimethyl formamide and acetonitrile, filtered by gravity, and precipitated by pouring into a large excess of methanol. After filtration and air drying, the copolymer was found to have a Kjeldahl nitrogen content of 24.2%. This corresponded to a 1/1 copolymer on a weight basis. The copolymer softened at $139\text{--}142^\circ$, on a Fisher-Johns melting point apparatus.

Distillation of N,N-bis(2-cyanoethyl)acrylamide to yield N-(2-cyanoethyl)acrylamide. A 5.0 g. sample of *N,N*-bis(2-cyanoethyl)acrylamide was distilled under reduced pressure in a small all glass low pressure distillation apparatus. At 150° and 1.9 mm. pressure, 2 g. of the material distilled over. The remainder of the product polymerized in the distilling pot to a hard, dark colored glass. A nitrogen analysis of the viscous liquid distillate indicated it to be *N*-(2-cyanoethyl)acrylamide. An infrared absorption spectrum on the distillate lent additional confirmation to this hypothesis (Fig. 1, R = H).

Anal. Calcd. for $\text{C}_6\text{H}_9\text{N}_3\text{O}$: N, 22.6. Found: N, 22.3.

Molecular weight: calcd. for $C_8H_8N_2O$, 124. Found: (microisopiestic) 150 ± 15 .

Acknowledgment. The authors are indebted to Miss E. C. Eberlin for the execution, interpretation, and reproduction of the infrared curves presented herein.

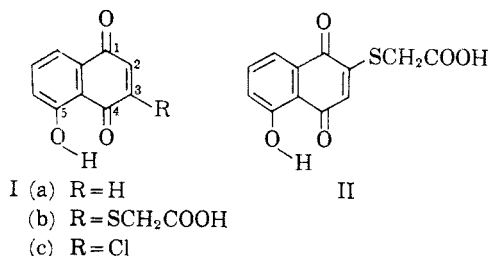
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Reaction of Juglone with Thioglycolic Acid

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The reaction of excess juglone (Ia) with thioglycolic acid affords only one of the two possible isomeric products, Ib and II, isolated in 73% yield.²



Structure Ib was assigned to this product (A) since it is also formed (in 39% yield) in the reaction of 3-chlorojuglone (Ic) with thioglycolic acid in the presence of pyridine. The reaction of juglone acetate with thioglycolic acid is reported to form only the acetate of the other isomer (B, isolated in 70% yield) to which structure II was assigned by exclusion. Since these results are opposite to those expected for nucleophilic addition,^{2,3} and observed for several other reactions, *e.g.* the reaction of 2,3-dibromojuglone and its acetate with aniline,⁴ a free-radical mechanism was suggested for the reactions with thioglycolic acid, and with *p*-thiocresol and *p*-toluenesulfonic acid for which similar

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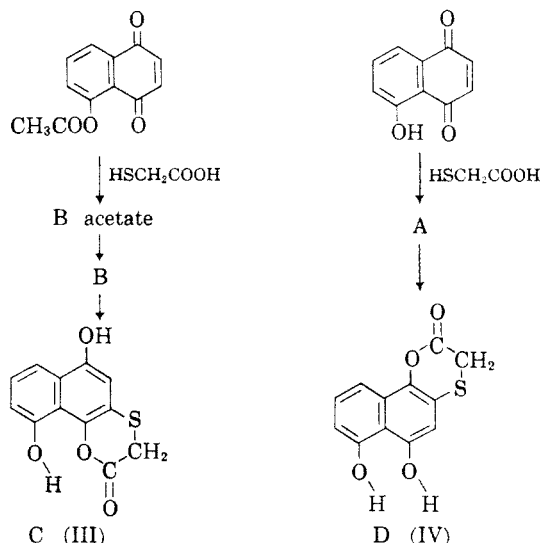
(2) R. H. Thomson, *J. Org. Chem.*, **16**, 1082 (1951).

(3) In additions to juglone acetate, conjugation of the unshared electrons of the phenolic oxygen at position 5 with the carbonyl group at position 4 opposes addition to the α,β unsaturated carbonyl system terminating at position 4 and hence 3-substituted derivatives are formed preferentially. This effect is also expected in additions to juglone, but is opposed by the effect of the intramolecular hydrogen bond between the hydroxyl group and the oxygen at position 4, which is expected to favor the accumulation of negative charge in the transition state at O-4 rather than O-2. In the nucleophilic reactions previously reported^{2,4} the latter effect predominates.

(4) R. H. Thomson, *J. Org. Chem.*, **13**, 377 (1948).

results were obtained.² No independent evidence was advanced in support of this hypothesis, which does not readily account for the observed orientations. The reaction of thioglycolic acid with 3-chlorojuglone may proceed by attack at either position 2 or 3 (each of which is the β position of an α,β unsaturated carbonyl system) followed by loss of HCl, leading to the formation of either Ib or II or a mixture of both. An unequivocal assignment of structures to the two isomers A and B was therefore desirable. This has been achieved by the reactions summarized in Scheme 1.

Scheme 1



Catalytic hydrogenation of isomer B,⁵ followed by treatment of the crude reaction mixture with *N,N'*-dicyclohexylcarbodiimide⁶ afforded compound C, $C_{12}H_{10}O_4S$, m.p. 193–203° (dec.), which could be identified as III and not IV on the basis of its effect in increasing the acidity of a boric acid solution. While naphthalene derivatives with free hydroxyl groups in the *peri*-positions (*e.g.*, IV) show an effect of unique magnitude in this test,⁷ compound C gave only a slight increase (Table I), attributable to the acidity of the phenolic hydroxyl groups. Since compound C is III, structure IV can be assigned to D.

Isomer A on hydrogenation and treatment with *N,N'*-dicyclohexylcarbodiimide was converted into a tan amorphous solid D. The behavior of D in the boric acid test (Table I) is in accord with its formulation as IV.

(5) The infrared spectrum of the residue from the mother liquor of crystallization of B acetate showed the presence of a few per cent of A acetate in the reaction mixture.

(6) Cf. R. B. Woodward, F. E. Bader, H. Bickel, A. J. Frey, and R. W. Kierstead, *J. Am. Chem. Soc.*, **78**, 2023 (1956).

(7) J. Boeseken, J. A. de Bruin, and W. E. van Rijswijk de Jong, *Rec. trav. chim.*, **58**, 3 (1939), cf. F. A. Hochstein, C. R. Stephens, L. H. Conover, P. P. Regna, R. Pasternack, P. N. Gordon, F. J. Pilgrim, K. J. Brunings, and R. B. Woodward, *J. Am. Chem. Soc.*, **75**, 5455 (1953).