

Catalysts Preparation.—The U. O. P. hydrogenation catalyst was obtained from Universal Oil Products Company, Riverside, Illinois. Raney nickel was purchased as an aqueous suspension from the Gilman Paint and Varnish Company, Chattanooga, Tennessee. The Ruffert nickel pellets and nickel catalyst supported in wax were obtained from The Ruffert Chemical Division of the Seymour Manufacturing Company.

Copper chromium oxide,² nickel on kieselguhr,³ nickel chromite⁴ and zinc chromite⁵ were prepared and used according to standard methods. Iron chromite and manganese chromite were prepared according to the method used for zinc chromite.

The boron phosphate on charcoal catalyst was prepared by mixing 58 g. of phosphoric acid (85%) and 30.9 g. of boric acid in 100 ml. of distilled water with vigorous stirring and heating at 85° for one hour. The mixture was evaporated to dryness with constant stirring on a hot-plate, the residue taken up in 200 ml. of distilled water and heated to boiling until a homogeneous suspension was obtained.

Fifteen grams of Darco activated charcoal were added with vigorous stirring and the suspension evaporated to dryness. The resulting cake was dried at 120° for twelve hours and then ground up for use.

The nickel-copper catalyst was prepared by dissolving 145.3 g. of nickel nitrate hexahydrate and 120.8 g. of cupric nitrate trihydrate in 1500 ml. of distilled water at 85°. One hundred seventy ml. of ammonium hydroxide, diluted with two parts of water, were added with vigorous mechanical stirring over a period of ten minutes while the temperature was maintained at 80–85°. Stirring and heating were continued fifteen minutes after which the suspension was

(2) Adkins, "Reactions of Hydrogen," University of Wisconsin Press, Madison, Wisconsin, 1937, p. 13.

(3) *Ibid.*, p. 19.

(4) Adkins, Richards and Davis, *THIS JOURNAL*, **63**, 1320 (1941).

(5) Sauer and Adkins *ibid.*, **59**, 1 (1937).

filtered on a Büchner funnel. The residue was washed three times by alternate suspension in hot water and filtration. After the last filtration the residue was sucked as dry as possible on the filter and then dried in an oven at 110° for three days. Before use the catalyst was reduced in a slow hydrogen stream at 450° for forty-five minutes.

Nickel formate was obtained from the Harshaw Chemical Company, Cleveland, Ohio. Before use, it was reduced at 350° in a slow hydrogen stream for one hour and then transferred directly to the reactor.

Method of Reaction.—The hydrogenations were carried out in a rocking bomb of 200 ml. void according to the method of Adkins.⁶ The reaction product was washed from the bomb with distilled water, made up to a known volume and aliquots analyzed for sodium formate by the method of Blackadder.⁷ Additional aliquots were acidified and used for the determination of Duclaux constants to demonstrate the presence of formic acid in the acidified product.

Summary

Sodium bicarbonate, in aqueous solution, has been converted to sodium formate by hydrogenation over ten different catalyst. Nickel-containing catalysts appear to be the most effective type among those tested. Catalyst concentration, hydrogen pressure, reaction temperature, reaction time and solution concentration have been shown to effect the conversion of sodium carbonate to sodium formate over a nickel catalyst.

(6) Adkins, "Reactions of Hydrogen," University of Wisconsin Press, Madison, Wisconsin, 1937, p. 40.

(7) Treadwell and Hall, "Analytical Chemistry," Vol. II, Ninth English Edition, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 561.

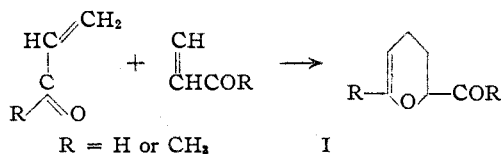
WYANDOTTE, MICHIGAN RECEIVED SEPTEMBER 15, 1948

[CONTRIBUTION NO. 56 FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TENNESSEE]

The Thermal Dimerization of Acrylonitrile¹

BY EUGENE C. COYNER^{2a} AND WILLIAM S. HILLMAN^{2b}

Various carbonylenic compounds, such as acrolein and methyl vinyl ketone, have been found by Alder and co-workers³ to undergo thermal dimerization to give up to 55 per cent. yields of dihydropyran derivatives of the type represented by structure I.



The present work was initiated with a view to carrying out this type of reaction with a nitrogen-containing analog, acrylonitrile, which it was thought, might correspondingly give a dihydro-

pyridine derivative. However, under the optimum conditions found for the thermal dimerization of acrylonitrile, the only dimeric products isolated were not heterocyclic in nature, but were found to be *cis*- and *trans*-1,2-dicyanocyclobutane. Both products, upon hydrolysis, gave *trans*-1,2-cyclobutanedicarboxylic acid, whose structure was established by conversion to the known dihydrazide and by its resolution into the *d* and *l* forms.

Experimental

1,2-Dicyanocyclobutane.—All runs were carried out in an externally heated steel bomb of 250 cc. capacity under autogenous pressures (20–130 atmospheres). About 0.1 g. of hydroquinone was added to inhibit chain polymerization. Representative reaction conditions and the yields of acrylonitrile dimer obtained are given in Table I.

TABLE I
DIMERIZATION OF ACRYLONITRILE

Acrylonitrile	53 ^a g.	53 g.	53 g.	100 cc.	100 cc.	100 cc.
Benzene, cc.	100	100	100			
Temp., °C.	245–250	275–280	295–304	195–200	200–210	245–265
Time, hours	7.5	2.0	0.5	24	3.5	0.8
Dimer, g.	1.5	2.6	2.4	5.5	1.2	2.8

^a A glass liner was used.

(1) Abstracted from a thesis by William S. Hillman submitted in partial fulfillment of the requirements for the M.S. degree.

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(3) Alder, Offermann and Rueden, *Ber.*, **74B**, 905 (1941); Alder and Rueden, *ibid.*, 920.

No significant differences in results were observed whether or not benzene was added or a glass liner was used. The dimerization reaction became excessively slow below 190°, and decomposition which produced carbonaceous residues occurred extensively above 300°.

After the heating cycle was completed, the reaction mixtures, which usually possessed a strong ammoniacal odor, were fractionally distilled. Unreacted acrylonitrile and the solvent, if any, were distilled at atmospheric pressure, and the residue was then distilled *in vacuo* through a 16 in. Vigreux-type column. The product was obtained in three colorless fractions of approximately the same weight.

TABLE II
FRACTIONS OF 1,2-DICYANOCYCLOBUTANE

Fraction number	B. p. at 3-4 mm.	M. p., °C.	Analyses			Molecular weight ^a
			C, %	H, %	N, %	
1	108-115°	< 0	67.54	5.91	26.55 ^b	106
2	120-125°	27				104
3	140-145°	62	67.58	5.55	26.39	101
Calcd. for C ₄ H ₆ N ₂ :			67.90	5.70	26.40	106

^a Determined ebullioscopically in benzene. ^b By difference.

It is probable that fractions 1 and 3 are the relatively pure *cis* and *trans* forms and that fraction 2 is a mixture of the two. All three fractions failed to react with bromine in carbon tetrachloride.

trans-1,2-Cyclobutanedicarboxylic Acid.—Fractions 1, 2 and 3 (see Table II) gave nearly identical yields (ca. 70-80%) of *trans*-1,2-cyclobutanedicarboxylic acid, m.p. 129-130°, upon hydrolysis in excess alcoholic potassium hydroxide or in 10% hydrochloric acid.

A typical alkaline hydrolysis was carried out as follows: To a solution of 10 g. of potassium hydroxide dissolved in 80 cc. of 70% ethyl alcohol was added 6 g. of fraction 1 of the dinitrile, m.p. < 0°. A bright blue color developed immediately which turned dark green in a few seconds and after a few minutes disappeared, leaving a colorless solution which was heated under reflux for twenty-four hours under a slow stream of nitrogen. The alcohol was then removed by distillation. The residue was made acidic with hydrochloric acid and was extracted with three 100 cc. portions of ether. Upon evaporation of the ether, a viscous liquid was obtained which solidified on cooling to give 5 g. (73%) of crude acid, m.p. 120-125°. After one recrystallization from concentrated hydrochloric acid it melted at 129-130°.

A typical hydrolysis with hydrochloric acid was carried out as follows: Five grams of dinitrile, fraction 2, m.p. 27°, was boiled under reflux with 100 cc. of 10% hydrochloric acid. The reaction mixture was extracted with ether and the ether was removed by evaporation. The yield of acid, m.p. 123-127°, was 5.6 g. (82%). After one recrystallization from concentrated hydrochloric acid it melted at 129-130°.

The isolation of only the *trans* isomer is not to be unexpected, since this acid is the more stable. Thus, if *cis*-1,2-cyclobutanedicarboxylic acid is heated in concentrated hydrochloric acid it is converted into the *trans* isomer.⁴ The *cis* dinitrile should be even more susceptible to isomerization.

Anal. Calcd. for C₄H₆O₄: C, 49.99; H, 5.60; neutral equivalent, 72. Found: C, 49.88; H, 5.55; neutral equivalent, 74.

The corresponding dihydrazide, *trans*-1,2-cyclobutanedicarboxydihydrazide, m.p. 219-220°, was prepared by the method of Buchman, *et al.*⁵

Anal. Calcd. for C₆H₁₂O₂N₄: C, 41.85; H, 7.02; N, 32.53. Found: C, 41.90; H, 7.07; N, 32.19.

(4) Bode, *Ber.*, **67B**, 332 (1934).

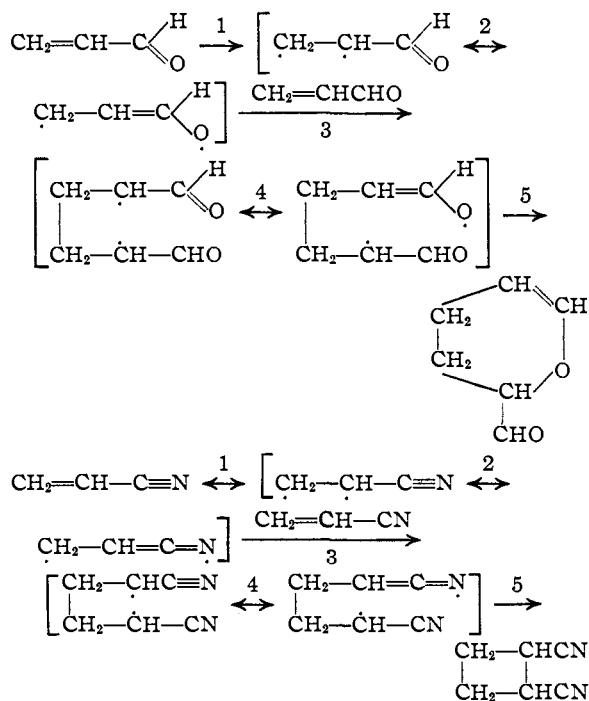
(5) Buchman, Reims, Skei and Schlatter, *THIS JOURNAL*, **64**, 2696 (1942).

Resolution of *trans*-1,2-Cyclobutanedicarboxylic Acid.—The resolution was carried out by the procedure of Goldsworthy,⁶ but, by employing a simple modification, a purer sample of the *l* isomer was obtained. To a solution of 7 g. of quinine in 25 cc. of ethyl alcohol was added a solution of 3 g. of *d,l*-*trans*-1,2-cyclobutanedicarboxylic acid in 200 cc. of water. The alcohol was then evaporated by boiling the mixture for forty-five minutes and the total volume was made up to 650 cc. with boiling water. The solution was cooled to 35° and the precipitated impure *l*-salt was removed by filtration. It was redissolved in hot water and allowed to crystallize at room temperature. The purified *l*-salt was removed by filtration and dried in air; it weighed 4 g. It was dissolved in 200 cc. of water and made alkaline with ammonium hydroxide. The solution was cooled to 0° and the quinine was removed by filtration. The filtrate was made acid with hydrochloric acid and extracted with ether. The ether extract was evaporated to dryness, leaving 0.5 g. of impure *l*-*trans*-cyclobutane-1,2-dicarboxylic acid which, after one recrystallization from benzene, melted at 114-117°. The specific rotation was -150° at 28° in water. This is a higher specific rotation than that reported by Goldsworthy⁶ (-124.3° at 30°), and thus represents a more complete resolution.

The mother liquor from the initial crystallization was concentrated to one-third of the original volume and the *d*-acid, in less pure condition, was separated as outlined above for the *l*-form. The melting point was 115-117° and the specific rotation at 28° was found to be +104°.

Discussion of Mechanism

Although the type of product obtained upon the thermal dimerization of acrylonitrile is quite different from the heterocyclic compounds obtained by Alder, *et al.*,³ from oxygen analogs, such as acrolein, it is probable that the mechanisms of the reactions involved are quite similar, as illustrated below:



According to Hurd,⁷ the primary effect of heat

(6) Goldsworthy, *J. Chem. Soc.*, **125**, 2012-2013 (1924).

(7) Hurd, *Ind. Eng. Chem.*, **26**, 54 (1934).

upon the C=C of an olefin is the rupture of one bond giving rise to a divalent radical $\dot{C}-\dot{C}$. In the examples given above this process is represented by step 1. The splitting of one electron pair of the double bond is doubtless facilitated in the compounds illustrated by resonance involving one of the unpaired electrons (process 2).

The establishment of a covalent bond between β -carbon atoms, as represented in step 3, is to be expected for two reasons. First, the most reactive center in the activated molecule (the di-radical) is the β -carbon atom, since the resonance involving the odd electron associated with the α -carbon atom and the oxygen atom in acrolein or the nitrogen atom in acrylonitrile (process 2) should make any reaction involving that electron less likely. Second, the new di-radicals thus formed can exist in four resonating forms, as partially illustrated by process 4, and hence are stabilized to some extent, whereas, if the initial union were between α -carbon atoms, no such resonance could occur. Similar considerations have been advanced by Koelsch and Boekelheide⁸

(8) Koelsch and Boekelheide, *THIS JOURNAL*, **66**, 413 (1944).

to account for the orientations observed in the coupling of aryl radicals with α,β -unsaturated compounds.

The final phase of the reaction (step 5) is a cyclization process. In the case of acrolein a relatively stable six-membered heterocyclic ring is formed. With acrylonitrile, however, the distribution of the odd electrons which would be required for the formation of a six-membered ring produces the linear configuration $C=C=N$, and the resulting distance between the atoms bearing the odd electrons is too great for electron pairing bond formation. The final electron pairing reaction therefore takes place between the two α -carbon atoms.

Summary

1. Acrylonitrile has been thermally dimerized to give low yields of 1,2-dicyanocyclobutane.
2. It is proposed that this reaction occurs by an electron pairing mechanism.
3. A similar mechanism is advanced for the thermal dimerization of acrolein and related carbonylenic compounds.

KNOXVILLE, TENNESSEE

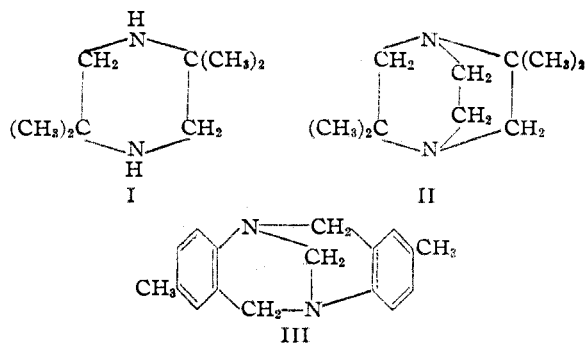
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[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

2,2,5,5-Tetramethylpiperazine and Derivatives

BY S. M. McELVAIN AND EVERETT H. PRYDE¹

The preparation of 2,2,5,5-tetramethylpiperazine (I) was undertaken in the hope that by bridging its nitrogens with an ethylene radical the bicyclic structure (II), which contains asymmetric nitrogen atoms comparable in structure to those of Troeger's base (III), might be obtained and resolved into its optical antipodes. The resolution of III² is the only recorded successful separation of a *dl*-mixture into its component optical isomers, the asymmetry of which is due to trivalent nitrogen atoms. Although the synthesis of II has not been achieved and further work in this direction is in progress in this Laboratory, the preparation



of I and the properties of certain of its derivatives seem of sufficient interest to report at this time.

The preparation of the dihydrochloride³ and the N,N' -dinitroso derivative⁴ of I in low yields have been reported, but none of these procedures appeared adaptable to the production of substantial quantities of I. For this reason it seemed that 2,2,5,5-tetramethyl-3,6-diketopiperazine (IV), if it could be obtained readily, offered a better approach to I.

The preparation of the diketopiperazine (IV) in 34% yield by heating methyl α -aminoisobutyrate⁵ and in 23% yield from the ethyl ester⁶ have been reported; however the requisite methyl ester was obtained in yields that left much to be desired.⁵ The preparation of IV from N -(α -aminoisobutyryl)- α -aminoisobutyric acid also has been reported.⁷ The ester approach⁵ to IV was investigated in the present work and, although a method of preparation of methyl α -aminoisobutyrate in good yield was developed, the product resulting from heating this ester contained only about 3% of

(3) (a) Reihlen, *et al.*, *Ann.*, **493**, 20 (1932); (b) Drew and Head, *J. Chem. Soc.*, 49 (1934).

(4) Conant and Aston, *THIS JOURNAL*, **50**, 2793 (1928).

(5) Franchimont and Friedman, *Rec. trav. chim.*, **27**, 197 (1908).

(6) Jacobson, *THIS JOURNAL*, **68**, 2628 (1946).

(7) Abderhalden and Gebelein, *Z. physiol. Chem.*, **152**, 125 (1926); Levene and Steiger, *J. Biol. Chem.*, **93**, 595 (1931).

(1) S. B. Penick and Company Fellow, 1947-1948.

(2) Prelog and Wieland, *Helv. Chim. Acta*, **27**, 1127 (1944).