cyanide[18] was added during a 1-hr. period. After holding for an additional 4 hr. at 40°, the mixture was cooled and the layers separated. Distillation of the oil layer gave 293 g., 87.5% yield, of 3-butenenitrile (b.p. 115/atm., lit.[19] b.p. 118.6°/763 mm., n_D^{30} 1.4015, d_{20}^{20} 0.8337, 98% purity by bromine titration).

3-Butenenitrile. Vapor phase process. A mixture of 306 g. (4 moles) of allyl chloride and 84 g. (3 moles) of 97% hydrogen cyanide was vaporized at a rate of 65 ml. per hr. through a preheater held at 100° into a stainless steel tube (1.0 in. inside diameter and 70 cm. in length) containing 350 cc. of 4 × 8 mesh copper aluminum oxide catalyst held at 150°. The reaction product was distilled to give unchanged starting materials and 69 g., a 34.5% yield based on hydrogen cyanide, of allyl cyanide (b.p. 115°, n_D^{30} 1.4022). The efficiencies were 34.5% and 42.5% based on recovered hydrogen cyanide and allyl chloride, respectively. Mass spectrographic analysis of the high boilers indicated a contained yield of 21% of 3-chlorobutyronitrile was also obtained.

3-Methyl-3-butenenitrile. A mixture of 1006 g. (11 moles) of methallyl chloride and 290 g. (10 moles) of 91% hydrogen cyanide was added during a 1.5-hr. period to a stirred mixture of 45 g. of cupric sulfate, 525 g. (5.25 moles) of calcium carbonate and 2500 ml. of water while maintaining a temperature of 30–40° by external cooling. After an additional 5 hr. at 40°, the mixture was filtered and extracted with diisopropyl ether. Distillation of the extract gave 764 g., 93% yield, of 3-methyl-3-butenenitrile (b.p. 76.5°/100 mm., lit.[20] b.p. 136.2–136.4°/atm., n_D^{30} 1.4143, d_4^{25} 0.8300).

2-Butenenitrile. 3-Butenenitrile (150 g.) was heated to reflux at about 120° with 1% by weight of basic catalyst and samples were removed periodically and titrated with 0.1N bromine/sodium bromide reagent in aqueous acidic methanol. The titration accurately measures unchanged 3-butenenitrile since the conjugated 2-butenenitrile does not add bromine under the conditions of analysis. Distillation of the final reaction mixtures gave *cis-* and *trans*-2-butenenitrile (b.p. 109–117°, n_D^{30} 1.4142–1.4168) containing about 2% of unchanged 3-butenenitrile. (See Fig. 1.)

3-Butenoic acid. To 134 g. (2 moles) of 3-butenenitrile held at 50° there was added with stirring 386 g. (4 moles) of concd. hydrochloric acid during a 1-hr. period. Heating was continued for 1 hr. at 50° before adding 500 ml. of water and heating at reflux for 1 hr. The cooled mixture was extracted with ether and the extract distilled to furnish some unchanged nitrile and the desired acid in 80% yield and 96% efficiency (b.p. 72–77°/20 mm., lit.[5] b.p. 69–70°/12 mm., n_D^{30} 1.4204; d_{20}^{20} 1.0087, 2.8% crotonic acid by infrared analysis).

Esters of 3-butenoic acid were prepared by the conventional acid-catalyzed azeotropic water removal method.

Addition of mercaptans to 3-butenenitrile. A mixture of 3-butenenitrile (2 moles) and a mercaptan (1 mole) was heated to about 70–100° in the presence of about 0.5% by weight of benzoyl peroxide and was irradiated by a General Electric Sunlamp for about 20–40 hr. Distillation of the reaction mixture gave the desired adducts plus unchanged starting materials. (See Table I) Absence of typical —CH_3 absorption at 7.3 μ[21] in the infrared spectrum indicated only terminal addition had occurred.

General procedure for oxidation of sulfides to sulfones. A mixture of sulfide (1 mole) and acetic acid (300 ml.) was stirred at 25° during the addition of a 20% solution of peracetic acid in ethyl acetate[16] (2.5 moles) over a 1-hr. period. Stirring at 25–27° was continued for an additional 3 hr., after which the mixture was either chilled and filtered to remove solid product or evaporated to yield a residual oil.

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[18] Liquid hydrogen cyanide was stored in glass, citrate-type pressure bottles which were chilled to 0° or below prior to opening. It was fed to the reaction vessel from brine-cooled feed tanks at 0° to −10°. All reactions, material transfers, and product layer distillations were conducted in an adequate fume hood, vented to the outside air. Aqueous wastes containing hydrogen cyanide were subjected to alkaline chlorination to oxidize the cyanides first to less toxic cyanates, then to harmless nitrogen and carbon dioxide.

[19] A. Christiaen, *Bull. soc. chim. Belges*, **34**, 147 (1925).

[20] M. Tamele, C. J. Ott, K. E. Marple, and G. Hearne, *Ind. Eng. Chem.*, **33**, 115–120 (1941).

[21] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd ed., John Wiley & Sons, Inc., New York, 1958, p. 13.

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, UNION CARBIDE CHEMICALS CO.]

Some Syntheses of 1,2,4-Butanetricarboxylic Acid[1]

JOHN W. LYNN AND RICHARD L. ROBERTS

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Several practical methods are described for the preparation of 1,2,4-butanetricarboxylic acid by nitric acid oxidation of 3-cyclohexenecarboxaldehyde and the related acid, nitrile, and ester.

The extensive use of polybasic acids in the manufacture of polymers, plasticizers, and lubricants has fostered considerable study of commercially feasible methods for their synthesis. Our studies are concerned with the oxidation of several 3-cyclohexene derivatives derived from Diels-Alder condensations[2] of butadiene with dienophiles such as acrolein, acrylic acid and acrylonitrile to give 1,2,4-butanetricarboxylic acid (V). Subsequent papers[3] describe the use of this tribasic acid in various syntheses.

The synthesis of 1,2,4-butanetricarboxylic acid

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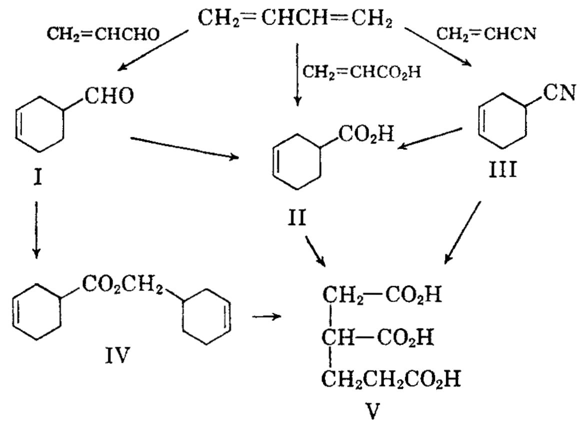
[1] Presented at The Gordon Research Conference, Organic Reactions and Processes, July 19, 1960.

[2] O. Diels and K. Alder, *Ann.*, **460**, 105 (1928).

[3] *J. Org. Chem.*, *in press.*

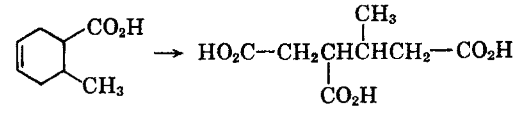
(V) by oxidation of 1-vinyl-3-cyclohexene,[4-6] 3-cyclohexenecarbonitrile,[7] 3-cyclohexenecarboxylic acid,[7] and 3-cyclohexenecarboxyaldehyde[8] have been reported. In general, low yields or uneconomical reaction conditions detract from the practicality of these methods.

The use of nitric acid as oxidant is particularly attractive since it exhibits adequate selectivity and the coproduct nitrogen oxides can, at least in part, be recovered for oxidation and recycle. Our earlier efforts using the conventional metal oxide catalysts were plagued by capricious induction periods, low yields and, in the case of 3-cyclohexenecarboxaldehyde (I), polymer formation. However, the use of a combination ammonium metavanadate and copper catalyst which was described by Lindsay[9] led to smooth reactions and gave much improved yields with little or no formation of residual byproducts. Oxidation of the related acid (II), nitrile (III), and Tishenko[10] ester (IV) also gave 1,2,4-butanetricarboxylic acid in satisfactory yield. A two-step oxidation of the aldehyde (I), first with oxygen and then with nitric acid, was also accomplished satisfactorily. These related syntheses are shown schematically below.

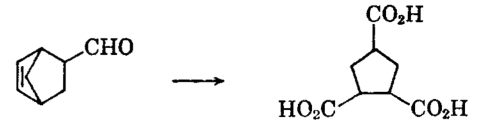


High yields of V may be obtained by chilling the reaction mixture to cause crystallization, removal of V by filtration, and recyclization of the filtrate to the reaction system after replenishing with nitric acid and starting olefin. We have recycled as many as five times with no indication of any by-product accumulation or need for additional catalyst. Apparently, all the by-products are converted to carbon dioxide and water.

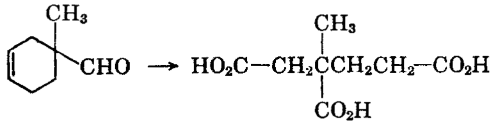
Nitric acid oxidation of 2-methyl-4-cyclohexenecarboxylic acid (VI), bicyclo[2.2.1]-5-heptene-2-carboxaldehyde (VIII), 1-methyl-3-cyclohexenecarboxaldehyde (X), and 3,4-cyclohexenedicarboxylic acid anhydride (XII) was also accomplished to yield 2-methyl-1,3,4-butanetricarboxylic acid (VII), 1,2,4-cyclopentanetricarboxylic acid (IX), 2-methyl-1,2,4-butanetricarboxylic acid (XI), and 1,2,3,4-butanetetracarboxylic acid (XIII).



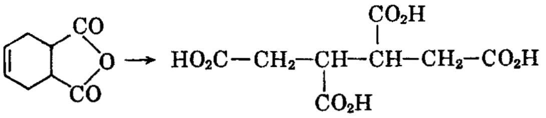
VI VII



VIII IX



X XI



XII XIII

Generally, the conditions found most suitable for oxidation of the substituted cyclohexenes to the polybasic acids were: 6 to 10 molar excess of 50–70% nitric acid, reaction temperature in the range of 50–70°, and a catalyst consisting of 0.1% of ammonium metavanadate and 0.25% of metallic copper powder, based on the weight of nitric acid. The olefin is added to the above mixture at a rate such that the heat of reaction may be easily dissipated by cooling. The triacid may be recovered by crystallization or conversion to distillable lower esters.

EXPERIMENTAL[11]

1,2,4-Butanetricarboxylic acid. (a) *From 3-cyclohexenecarboxaldehyde* (I). A mixture of 10 moles of 70% nitric acid, 0.1% by weight of ammonium metavanadate, and 0.25% by weight of powdered metallic copper was stirred and heated to 56°. While maintaining a reaction temperature of 50–60° by cooling, 3-cyclohexenecarboxaldehyde (I) (1 mole) was added dropwise to the stirred mixture over a period of 1.5 hr. The mixture was held at 50–60° for an additional 4 hr., then chilled to approximately −5°. During the course of the reaction, effluent gases containing nitrogen oxides were fed to a scrubbing system where the contained nitric oxide and nitrogen dioxide were converted to recoverable nitric acid

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(4) V. Lebedew and A. G. Skawronskaya, *J. Phys. Chem.* (*U.S.S.R.*), **43,** 1127.

(5) J. C. Conly, *J. Am. Chem. Soc.*, **75,** 1148 (1953).

(6) R. H. Perry, Jr., *Ozonolysis of Vinylcyclohexene*, Paper #61, Division of Petroleum Chemistry, 137th Meeting, American Chemical Society.

(7) Brit. Patent **510,638** (I. G. Farbinindustrie Aktiengesellschaft).

(8) Brit. Patent **688,344** [Naamlooze Venootschap De Bataafsche Petroleum Maatschappij (The Netherlands)].

(9) A. F. Lindsay, *Chem. Eng. Sci. Spec. Suppl.*, **8,** 78 (1954).

(10) Brit. Patent **713,639** (Distillers Co. Ltd.).

(11) All temperatures are uncorrected.

by oxidation and absorption in water. Crystalline V (80 g., 98.7% purity by titration, m.p. 117°, reported[12] m.p. 121°), yield of 41.6%, was filtered from the chilled reaction product mixture and dried under reduced pressure. The filtrates, containing unused nitric acid and additional dissolved I, were stripped of excess water by distillation under reduced pressure, then recharged to the reaction vessel. Enough 70% nitric acid was added to bring the total contained nitric acid to 10 moles, the mixture was heated to 50–60°, and the addition of I was carried out as before. This cycle was repeated a total of five times, after which the final filtrates were stripped of most of the remaining unchanged nitric acid by repeated passage through a tubular vapor-lift, steam-heated, flash evaporator. The concentrated sirup remaining was then esterified with ethanol in a conventional manner to convert the contained organic acids to their ethyl esters. Distillation gave a small fraction containing ester of lower molecular weight acids, but the main fraction was identified as triethyl 1,2,4-butanetricarboxylate (b.p. 137°/2 mm.; reported[13] b.p. 162°/6 mm.; n_D^{30} 1.4351).

Anal. Calcd. for $C_{13}H_{22}O_6$: C, 56.92; H, 8.08. Found: C, 57.23; H, 7.96.

Including the triethyl ester, the total yield to contained V over the series of five runs was 74.4%.

(b) *From 3-cyclohexenecarboxaldehyde by two-step catalytic-nitric acid oxidation.* There were charged to the reactor 550 g. (5 moles) of I, 550 g. of water, and 1.1 g. of cobalt acetate. The temperature was maintained at 20° and oxygen was diffused into the liquid at the rate of 880 cm.^{3} per minute, while the mixture was stirred for 3 hr. (Oxygen or air may be used.) Absorption of the gas was virtually complete at first, but as the reaction proceeded the amount of blow-off increased. Unchanged I (247 g.) was recovered by azeotropic distillation. The crude stripped residue contained 264 g. (2.1 moles) of 3-cyclohexenecarboxylic acid (II). (The residue was a mixture with 62.8% of II and the remainder unidentified material.) The yield for the reaction was 42% and the efficiency 76.4%. The mixture was then oxidized with nitric acid in the manner previously described to give 140 g. of crystalline product (95.7% acid as V, m.p. 114–116°). The filtrates from crystallization and washing of the solid product were then esterified with an excess of ethanol to yield 100 g. of triethyl 1,2,4-butanetricarboxylate. This represents a total yield of 85.0%, based on the contained II in the starting material, at an over-all efficiency of 65% from I.

(c) *From 3-cyclohexenecarboxylic acid* (II). 3-Cyclohexenecarboxylic acid (II) was oxidized with nitric acid in the manner described above to give V in 85% yield.

(d) *From oxidation of 3-cyclohexenemethyl 3-cyclohexenecarboxylate* (IV).[10] The nitric acid oxidation was accomplished in the manner described above to give V in 62% yield.

(e) *From 3-cyclohexenecarbonitrile* (III). The oxidation of III with nitric acid was accomplished in the manner described above but without the use of metallic copper as cocatalyst to give V in 78.5% yield when isolated as triethyl ester.

Triethyl 2-methyl-1,3,4-butanetricarboxylate. The oxidation of 2-methyl-4-cyclohexenecarboxylic acid (VI) with nitric acid was accomplished in the manner described previously to give VII in 61% yield when isolated as the triethyl ester (b. p. 127–137°/0.9 mm., n_D^{30} 1.4372, d_{20}^{20} 1.0637).

Anal. Calcd. for $C_{14}H_{24}O_6$: C, 58.31; H, 8.39. Found: C, 58.14; H, 8.19.

1,2,3,4-Butanetetracarboxylic acid (XIII). The oxidation of 3,4-cyclohexenedicarboxylic anhydride (XII) with nitric acid was accomplished in the manner previously described to give a 68% yield of XIII [m.p. 185° and 234°, reported[14] m.p. 189° (*meso*) and 236° (*dl*)].

Anal. Calcd. for $C_8H_{10}O_8$: C, 41.03; H, 4.31. Found: C, 41.20; H, 4.38.

1,2,4-Cyclopentanetricarboxylic acid (IX). The nitric acid oxidation of bicyclo[2.2.1]-5-heptene-2-carboxaldehyde (VIII) was accomplished in the manner described above to give a 29.2% yield of IX (m.p. 138–145° from methyl ethyl ketone and benzene, reported[15] m.p. 124–130° (*trans*) and 146–148° (*cis*), purity 99% by titration with 0.5*N* sodium hydroxide).

Anal. Calcd. for $C_8H_{10}O_6$: C, 47.53; H, 4.99. Found: C, 47.25; H, 4.68.

Esterification with ethanol in the conventional manner gave triethyl 1,2,4-cyclopentanetricarboxylate as a light amber, oily mixture of isomers (119°/0.5 mm.–140°/0.8 mm.; n_D^{30} 1.4398–1.4460; purity 98.2% by saponification).

Anal. Calcd. for $C_{14}H_{22}O_6$: C, 58.73; H, 7.75. Found: C, 57.90; H, 7.70.

Triethyl 2-methyl-1,2,4-butanetricarboxylate. Oxidation of 3-cyclohexene-1-methylcarboxaldehyde (X) in the manner previously described gave a 60% yield of XI which was isolated as the triethyl ester (b.p. 103–116°/0.2 mm., n_D^{30} 1.4370, purity 86% by saponification).

Anal. Calcd. for $C_{14}H_{24}O_6$: C, 58.31; H, 8.39. Found: C, 57.79; H, 8.15.

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SOUTH CHARLESTON, W. VA.

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[12] J. G. T. Brown, J. D. Rose, and J. L. Simonsen, *J. Chem. Soc.*, 101, 1944.

[13] S. F. Birch, W. J. Oldham, and E. A. Johnson, *J. Chem. Soc.*, 818 (1947).

[14] K. Alder and M. Schumacher, *Ann.*, **564**, 96–109 (1949).

[15] L. J. Goldsworthy and W. H. Perkin, *J. Chem. Soc.*, **105**, 2671 (1914).