isopropyl alcohol, had m. p. 214° with decomposition. Hasselstrom and Hampton reported 199–200°, probably the optically inactive product; yield 11 g. (31.3%). The product was soluble in either dilute sodium hydroxide or dilute hydrochloric acid.

Anal. Calcd. for $C_{12}H_{19}O_3N_3$: neut. equiv., 253.3. Found: neut. equiv., 254.0.

1-Apocamphane-β-ethanol (VIII).—A solution of 367 g. of 2-chloro-1-apocamphane-β-ethyl acetate in 2 l. of butanol was saponified with 75 g. of sodium hydroxide in 75 ml. of water. After it was washed with water and dehydrated the butanol solution was diluted with 2 l. of additional butanol and was treated with 460 g. of sodium in small portions over a period of two weeks. The solution was washed free of sodium salts with hydrochloric acid and water. After removing butanol by distillation at atmospheric pressure the product was fractionated at 10 mm. pressure through a 60 × 2.5 cm. Stedman column. The main fraction, b. p. 121–122°, weighed 113.4 g. (44.9% yield); f. p. 33°; n^{40}_D 1.4818; d^{40}_4 0.9633; $[\alpha]^{25}_D$ 0.00; M_D, calcd. 50.12, found 49.79. The product was identified by its oxidation to 1-apocamphaneacetic acid (see below). 1-Apocamphane-β-ethanol was characterized by conversion to the 1-naphthylurethan, m. p. 81.2°.

Anal. Calcd. for $C_{22}H_{27}O_2N$: N, 4.15. Found: N, 4.02.

The acid phthalate was also prepared; m. p. 147–149°.

Anal. Calcd. for $C_{19}H_{24}O_4$: neut. equiv., 316.4. Found: neut. equiv., 312.2.

1-Apocamphaneacetic Acid (IX).—(a) By oxidation of 1-apocamphane-β-ethanol with chromic anhydride in acetic acid a practically quantitative yield of the crude acid was obtained. After recrystallization from aqueous methanol it melted at 75.4°. No melting point depression occurred upon mixing with an authentic sample of 1-apocamphaneacetic acid prepared by the method of Hasselstrom and Hampton.[2] Neut. equiv., calcd. 182.25, found 182.3. The *p*-phenylphenacyl ester was prepared in the usual way and melted at 85–86°.

Anal. Calcd. for $C_{25}H_{28}O_3$: C, 79.75; H, 7.50. Found: C, 79.3; H, 7.7.

(b) 1-Apocamphaneacetic acid was also prepared by modified Wolff–Kishner decomposition of the semicarbazone of 2-keto-1-apocamphaneacetic acid. To a solution of 5 g. of sodium in 50 ml. of methanol and 50 ml. of triethylene glycol there was added 6 g. of the semicarbazone. The mixture was heated to 200°, the methanol being allowed to distil. It was held at 200° for four hours, cooled, dissolved in 100 ml. of water and 40 ml. of hydrochloric acid and extracted with ether. The semi-crystalline paste obtained upon evaporation of the ether was distilled at 10 mm. to yield 1.6 g. (37% yield) of crude 1-apocamphaneacetic acid, which upon recrystallization from aqueous methanol melted at 73–74.5°. Its identity was confirmed by mixed m. p. comparison with an authentic sample of 1-apocamphaneacetic acid. Its *p*-phenylphenacyl ester melted at 84–85° and showed no m. p. depression on mixing with an authentic sample.

Summary

Nopyl acetate readily reacts with hydrogen chloride or bromide to yield new compounds of the apocamphane series. New compounds produced include 2-chloro- and 2-bromo-1-apocamphane-β-ethyl acetate, the corresponding 2-halo-1-apocamphane-β-ethyl alcohols, the corresponding 2-halo-1-apocamphaneacetic acids and 1-apocamphane-β-ethanol. The previously known lactones of 2-hydroxy-1-apocamphaneacetic acid, 2-keto-1-apocamphaneacetic acid, and 1-apocamphaneacetic acid, were prepared by new routes.

All of the compounds that are asymmetric are believed to be the optically pure levo isomers.

By means of the series of reactions described here the naturally occurring optically pure *l*-β-pinene has been converted to optically pure *l*-camphene.

Jacksonville, Florida Received[5] January 27, 1950

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(5) The original version of this manuscript was received on October 25, 1948.

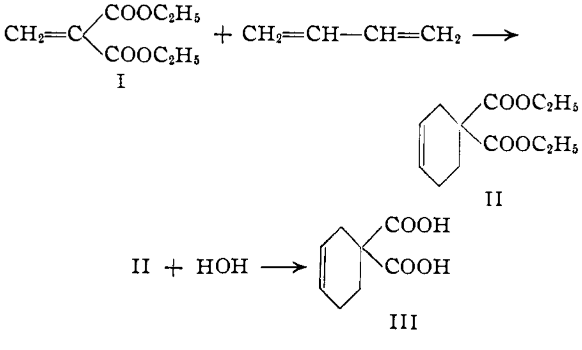
[Contribution from The B. F. Goodrich Company, Research Center, Brecksville, Ohio]

Vinylidene Cyanide. II. The Synthesis from 4,4-Dicyanocyclohexene

By A. E. Ardis, S. J. Averill, H. Gilbert, F. F. Miller, R. F. Schmidt, F. D. Stewart and H. L. Trumbull

The previous paper of this series[1] described the preparation of monomeric vinylidene cyanide from 1,1,3,3-tetracyanopropane and from 1,1-dicyanoethyl acetate. This paper describes a third synthesis of vinylidene cyanide by the pyrolysis of 4,4-dicyanocyclohexene.

The pyrolysis of cyclohexene and substituted cyclohexenes has been discussed by Norton[2] under the name of "reverse diene synthesis." An unbridged cyclohexene gives a conjugated diene and an olefin upon pyrolysis. These pyrolysis products can usually be recombined via the Diels–Alder reaction to give the original cyclohexene. The series of reactions presented here indicates a novel use of the "reverse diene synthesis," whereby a reactive ethylenic compound, *e. g.*, (I), may undergo group substitution or modification without regard to the reactivity of the double bond. The preparation of vinylidene cyanide from 4,4-dicyanocyclohexene illustrates this use of the "reverse diene synthesis."



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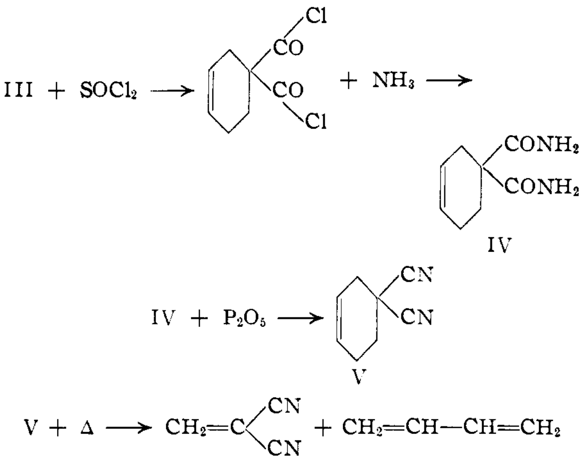
(1) A. E. Ardis, *et al.*, This Journal, **72**, 1305 (1950).

(2) J. A. Norton, *Chem. Revs.*, **31**, 495 (1942).



An analogous set of reactions can be carried out starting with ethyl α-cyanoacrylate (VI) and butadiene-1,3.[1,3] Attempts to prepare an amide from either ester I or VI proved unsuccessful, which is consistent with the fact that these esters are polymerized by both water and bases. In both cases the amide dehydration would be difficult to perform on the ethylenic amide because of the great tendency to polymerize of the vinylidene cyanide formed. The synthesis through the Diels–Alder adduct avoids these difficulties.

Experimental

4,4-Dicarboxycyclohexene.—Two hundred forty-three grams of potassium hydroxide was dissolved in 84 g. of water in a three-liter, three-necked flask, fitted with stirrer, separatory funnel and reflux condenser. To this was added 1,400 ml. of ethanol and the solution heated to a gentle reflux. While refluxing and stirring this mixture 245 g. of 4,4-dicarbethoxycyclohexene (prepared according to the directions of Bachman[4] and Tanner) was added dropwise. The reaction mixture was then refluxed for an additional two hours. At the end of this time the mixture was cooled and the solid which formed was collected on a filter. The solid was dissolved in a minimum amount of water, and concentrated hydrochloric acid was added using four times the amount required to make the mixture acid to litmus. The acidified mixture was then extracted with ether and the extract dried over anhydrous calcium chloride. The extract was filtered, evaporated to half its volume and hexane added to cause precipitation. One hundred sixteen grams of crystalline product was collected, m. p. 187–190°.

Anal. Calcd. for $C_8H_{10}O_4$: C, 56.46; H, 5.91. Found: C, 56.43; H, 5.93.

4,4-Dicarbamylcyclohexene.—Twenty-two grams of 4,4-dicarboxycyclohexene was mixed with 120 ml. of thionyl chloride (E. K. Co. White Label) and heated under reflux for twenty-seven hours. The excess thionyl chloride was then distilled off and the residue diluted with four times its volume of dry ether. This solution was then added dropwise to an ice-cold solution of ammonia in dry ether. Ammonia was bubbled into the mixture during this addition to keep it saturated. The mixture was allowed to stand overnight, then the solid material was filtered off. The solid was dried in air and washed with sufficient water to dissolve out the ammonium chloride. The product was recrystallized from methanol, m. p. 234–236°; weight 15 g.

Anal. Calcd. for $C_8H_{12}O_2N_2$: C, 57.12; H, 7.19; N, 16.65. Found: C, 57.13; H, 7.17; N, 16.44.

4,4-Dicyanocyclohexene.—Forty-five grams of 4,4-dicarbamylcyclohexene, 70 g. of phosphorus pentoxide, and sufficient tricresyl phosphate to make a fluid slurry were placed in a 500-ml. distilling flask and evacuated to 2 mm. A bath, previously heated to 200°, was elevated to immerse the flask and the bath temperature was then increased to 250–260°. The product, 22 g., which distilled over was collected in an ice-cooled receiver, m. p. 35.0–35.5°. This melting point is the same as that obtained using the methods of preparation in paper I of this series.

Pyrolysis of 4,4-Dicyanocyclohexene.—Seventy-two grams of 4,4-dicyanocyclohexene was distilled through a 15-mm. i. d. brass tube at red heat under a pressure of 8 mm., and 26.5 g. of product was collected in an ice-cooled receiver. It is desirable to use clean, dry apparatus and to stabilize the monomeric vinylidene cyanide by the presence of a small amount of phosphorus pentoxide in the receiver. This was distilled to give 5.2 g. of vinylidene cyanide, b. p. 35–38° (1 mm.), m. p. 9.2°.

Acknowledgment.—The microanalyses for carbon, hydrogen and nitrogen were performed by J. R. Kubik and A. K. Kuder.

Summary

1. 4,4-Dicyanocyclohexene has been prepared from 4,4-dicarbethoxycyclohexene through the diacid and di-amide.

2. Vinylidene cyanide has been prepared from 4,4-dicyanocyclohexene by pyrolysis.

BRECKSVILLE, OHIO RECEIVED JANUARY 16, 1950

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[3] A. E. Ardis, U. S. Patents 2,467,926-7 (1949).

[4] G. B. Bachman and H. A. Tanner, *J. Org. Chem.*, **4**, 493 (1939).