

crystallizations from ethanol. The ultraviolet absorption spectrum of the 2,4-dinitrophenylhydrazone of VII in 95% ethanol had a prominent maximum at 361 $m\mu$ ($\epsilon = 23,400$).

Anal. Calcd. for $C_{13}H_{12}O_4N_4$: C, 54.16; H, 4.20. Found: C, 54.44; H, 4.36.

Treatment of 12.8 g. (0.12 mole) of XI dissolved in 10 g. of pyridine at 0° with 14.0 g. (0.12 mole) of thionyl chloride gave 2.8 g. (19%) of a chloride, b. p. 47.5–48.5° (11 mm.) which had n_D^{25} 1.4932. The chloride appeared to be largely 3-chloronorbornylene on the basis of its infrared spectrum (Fig. 3) which showed very strong absorption at 12.2–12.8 μ . On quantitative hydrogenation in ethyl acetate the material absorbed 19% of the theoretical quantity of hydrogen for a dehydronorbornyl chloride.

The reaction at 0° of 11 g. (0.10 mole) of XI dissolved in 50 ml. of ether containing 5 g. of dry pyridine with 12.4 g. (0.046 mole) of phosphorus tribromide gave 3.2 g. (19%) of a monobromide, b. p. 63–67° (14.3 mm.), with n_D^{25} 1.5210. The infrared spectrum (Fig. 3) of the product indicates that it is largely II since all the strong absorption bands of II are present. A number of bands correspond fairly well to bromide VIII although the absorptions at 5.8, 7.2, 9.0, 9.6 and 12.9 μ do not appear in the spectra of either II or bromide VIII and may be due to *exo*-dehydronorbornyl bromide (XV) which has not as yet been obtained as a pure substance. The reaction product may be largely II and XV or a mixture of II, VIII and XV.

Preparation of *exo*-Dehydronorborneol (XII).—The method was adapted from the work of Doering and Aschner.²⁰ A mixture of 5 g. of crude XI, 10 ml. of dry toluene, 0.1 g. of fluorenone and a small piece of sodium was refluxed for seventeen hours. The reaction products were poured into water and the organic layer separated and dried over magnesium sulfate. The toluene was evaporated under reduced pressure and the residue sublimed. The crude product was recrystallized from pentane (Skau tube); yield 1.8 g. (36%), m. p. 97.5–99.2°.

XII reacted with phenyl isocyanate to give the phenylurethan; m. p. 152.4–153.6° after several crystallizations from hexane.

Anal. Calcd. for $C_{14}H_{16}O_2N$: C, 73.34; H, 6.59. Found: C, 73.55; H, 6.82.

The structure of the urethan was established by hydrogenation in ethyl acetate over platinum oxide to the phenylurethan of β -norborneol; m. p. 140.6–141.4° (lit., 139–140°)²¹ after crystallization from hexane.

The infrared spectrum of XII is shown in Fig. 2.

Attempted Isomerization of 3-Hydroxynorbornylene (V), *endo*- and *exo*-Dehydronorborneols (XI and XII).—

One to two gram samples of the alcohols were shaken with 10 ml. of aqueous 25–50% sulfuric acid at room temperature for sixteen hours. Water was added and the mixture extracted with ether. The ethereal extract was shaken with dilute sodium hydroxide solution, then with water and finally dried over magnesium sulfate. The ether was distilled and the residue fractionally sublimed. In each case, the first fraction was alcohol while the second fraction was glycol. The alcohol fractions were analyzed by their infrared spectra in carbon disulfide solutions. With 25% acid only unchanged alcohol was recovered. With 30–35% acid the starting material and considerable glycol were obtained while using 40% acid only glycol was isolated. With 50% acid no solid products were obtained. The glycol from V, XI and XII had m. p. 169.5–171°.

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: C, 65.73; H, 9.53.

***t*-Butylbenzene and Norbornylane with N-Bromosuccinimide.**—A mixture of 15 g. (0.112 mole) of *t*-butylbenzene, 15 g. (0.085 mole) of N-bromosuccinimide, 0.1 g. of benzoyl peroxide and 100 ml. of carbon tetrachloride was stirred and refluxed under a General Electric RS Sunlamp for twenty-eight hours. The solution became dark but on filtration 13.8 g. (92%) of the N-bromosuccinimide was recovered.

A mixture of 10 g. (0.104 mole) of bicycloheptane, 19 g. (0.106 mole) of N-bromosuccinimide, 0.1 g. of benzoyl peroxide, and 50 ml. of carbon tetrachloride was stirred and refluxed under an ultraviolet lamp for two hours. Only a 4% yield of an impure bromide, b. p. 86–90° (45 mm.), was obtained.

Summary

The reaction of norbornylene with N-bromosuccinimide, bromine, or bromine and pyridine was found to give 3-bromonorbornylene.

3-Bromonorbornylene was converted to the corresponding hydrocarbon, alcohol, and carboxylic acid. The *endo*-dehydronorbornyl halides appear to isomerize at 160–195° in steel containers to 3-halonorbornylenes. The *endo*-dehydronorbornyl halides give the same reaction products as 3-bromonorbornylene *via* hydrolysis or the Grignard reagents.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE GLIDDEN COMPANY—NAVAL STORES DIVISION]

Nopol. II. Syntheses in the Apocamphane Series. The Preparation of Optically Pure *l*-Camphene

BY JOSEPH P. BAIN, ALBERT H. BEST, BURT L. HAMPTON, GEORGE A. HAWKINS AND LELAND J. KITCHEN

There was recently described¹ the preparation and certain reactions of nopol (I), (6,6-dimethylbicyclo[3.1.1].2-heptene-2-ethanol), the bicyclic alcohol produced by the condensation of β -pinene with formaldehyde. Since β -pinene occurs only in the optically pure levo form and nopol produced under various conditions always possesses substantially the same optical rotation (–36.1° for 10-cm. tube) it is assumed that nopol is also an optically pure levo compound and is not readily racemized. It was shown that

(1) Bain, THIS JOURNAL, 68, 638 (1946).

nopol possesses the α -pinene rather than the β -pinene structure, though it can be prepared only from β -pinene. Nopol and its esters undergo a number of reactions which have been applied to α -pinene. It is our purpose to describe here the reaction of nopyl acetate (II) with anhydrous hydrogen chloride to yield 2-chloro-1-apocamphane- β -ethyl acetate (III) and with hydrogen bromide to form the corresponding 2-bromo compound either of which may be converted to *l*-camphene by means of reactions to be described. It is considered that the addition of hydrogen

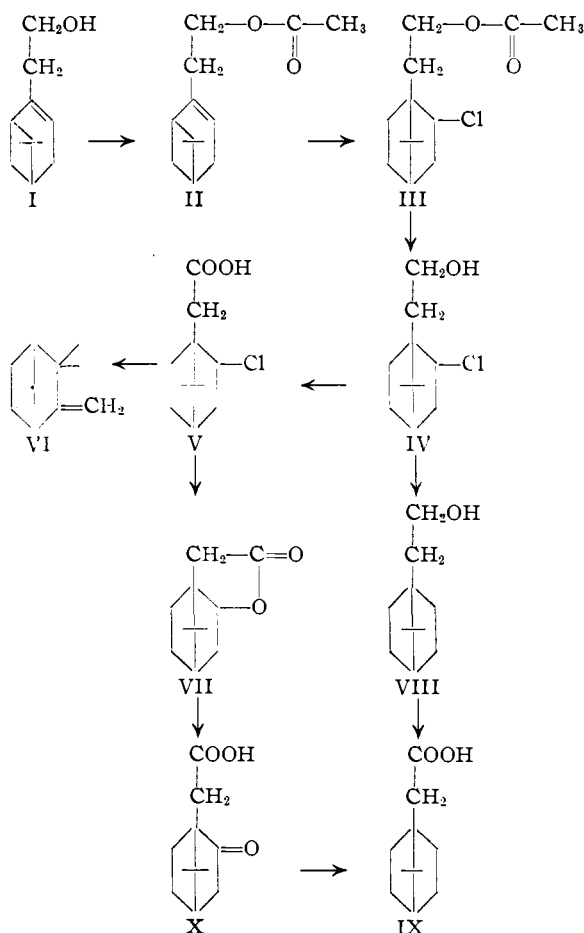
chloride to nopyl acetate is analogous to the addition of hydrogen chloride to α -pinene to yield bornyl chloride and therefore that these new apocamphane compounds are of the *trans* series.

A solution of nopyl acetate (II) in an inert solvent absorbs about two moles of hydrogen chloride, one of which is removed readily by a water wash leaving III.

On saponification of III the corresponding chloroalcohol (IV) is formed. On dechlorination 1-apocamphane- β -ethanol (VIII) is obtained which may be oxidized to 1-apocamphaneacetic acid (IX), a known² compound.

On oxidation of 2-chloro-1-apocamphane- β -ethanol (IV), 2-chloro-1-apocamphaneacetic acid (V) is obtained. The sodium salt of this acid decomposes on warming to pure *l*-camphene (VI) and the lactone of 2-hydroxy-1-apocamphaneacetic acid (VII) which has been prepared previously² but probably in the optically inactive form.

The lactone VII on saponification and oxidation with potassium permanganate yields the 2-keto acid (X) which is converted to 1-apocamphaneacetic acid (IX) by a modified Wolff-Kishner reduction.



(2) Hasselstrom and Hampton, *This Journal*, 61, 3445 (1939).

Finally, 2-chloro-1-apocamphaneacetic acid (V) is dechlorinated to the optically inactive 1-apocamphaneacetic acid (IX) by sodium in liquid ammonia.

The usual methods of preparing camphene yield more or less racemized material frequently containing appreciable amounts of impurities such as tricyclene which are formed during the preparative reaction and which are difficult to separate from the desired product. The preparation of *l*-camphene from nopol as described here apparently involves no conditions leading to racemization of the final product or of intermediates. Further, the decomposition of 2-chloro-1-apocamphaneacetic acid (V) appears to yield *l*-camphene and the lactone of 2-hydroxy-1-apocamphaneacetic acid (VII) exclusively so that there is no difficulty in isolating the pure *l*-camphene.

The raw material for this synthesis of *l*-camphene is the naturally occurring *l*- β -pinene from gum or sulfate turpentine which is known to be optically pure. In view of these facts and the fact that our *l*-camphene possesses the highest optical rotation reported, we consider the compounds whose preparation are described here to be optically pure *levo* forms although this has not been rigorously proven.

Experimental

2-Chloro-1-apocamphane- β -ethyl Acetate (III).—A solution of nopyl acetate¹ (104 g. or 0.46 mole) in 428 ml. of ethylene chloride was maintained at 2 to 10° while hydrogen chloride was passed in until absorption was complete. The solution was allowed to warm to room temperature overnight and weighed. The weight increase amounted to 35 g. (0.96 mole of hydrogen chloride). On washing the solution with water 15.3 g. of hydrogen chloride was removed thus leaving 19.7 g. or 0.54 mole of bound hydrogen chloride (117% of theory required for formation of III). The ethylene chloride was evaporated and the product distilled at 135 to 150° at 2 to 6 mm. with some decomposition. The crystalline distillate, recrystallized three times from methanol, melted at 62–63°, $[\alpha]_D^{25} -27.3^\circ$ (2.5% in 95% ethanol).

Anal. Calcd. for $C_{13}H_{21}O_2Cl$: Cl, 14.49. Found: Cl, 14.40, 14.55.

Subsequent experiments showed that improved yields were obtained by eliminating the distillation step. Evaporation of the crude III in methanol followed by the solution of the crude III in methanol, cooling the solution to –30° and seeding provided yields of 70 to 75% of once crystallized material melting at 57 to 60°.

2-Bromo-1-apocamphane- β -ethyl Acetate.—A solution of 300 g. of nopyl acetate in 1 l. of ethylene chloride was saturated with hydrogen bromide at 0°. After standing overnight and washing with water followed by dilute sodium carbonate, the ethylene chloride was evaporated to yield a viscous brown oil which partly congealed in the ice-box. The crystalline product was filtered from the oil and washed with cold methanol. An additional small crop of crystals was obtained from the mother liquor after it was diluted with an equal volume of methanol and refrigerated at 0°. A total of 117 g. (28.1%) of crude crystalline product was obtained which, after three recrystallizations from methanol, melted at 52.2–52.4°.

Anal. Calcd. for $C_{13}H_{21}O_2Br$: Br, 27.63. Found: Br, 27.09, 27.36.

2-Chloro-1-apocamphane- β -ethanol (IV).—A solution of 150 g. of 2-chloro-1-apocamphane- β -ethyl acetate

(III) in 500 ml. of methanol was saponified with a solution of 38 g. of potassium hydroxide in 50 ml. of water at room temperature in about fifteen hours. The product was isolated by diluting the saponification mixture with water and extracting with ether. The partly solidified residue from evaporation of the ether was dissolved in an equal volume of hexane, cooled to -10° , and filtered. After recrystallization from the same solvent the product weighed 106.5 g. (85.7% yield) and melted at $37.5-38.5^{\circ}$. Repeated crystallizations raised the m. p. to $39.8-40.6^{\circ}$; $[\alpha]^{25}_{\text{D}} -35.6^{\circ}$ (9.9% in 95% ethanol).

Anal. Calcd. for $\text{C}_{11}\text{H}_{19}\text{OCl}$: Cl, 17.49. Found: Cl, 17.54, 17.53.

A subsequent experiment showed that purification of the crude alcohol could be accomplished most conveniently by distillation at 1–2 mm.

The 1-naphthylurethan of IV was prepared in the usual manner in practically quantitative yields. After recrystallizations from heptane and ethanol it melted at $96.5-97.5^{\circ}$.

Anal. Calcd. for $\text{C}_{22}\text{H}_{26}\text{O}_2\text{NCl}$: N, 3.77. Found: N, 3.73.

2-Chloro-1-apocamphaneacetic Acid (V).—To a solution containing 550 g. of chromic anhydride, 2.5 l. of acetic acid, 1.0 l. of water and 500 ml. of concentrated sulfuric acid there was added with stirring and cooling 730 g. of 2-chloro-1-apocamphane- β -ethanol (IV) at such a rate that the temperature did not exceed 20° . About fifteen hours was required for the addition. After standing twenty-four hours the solution was diluted with 3 l. of water and extracted with 5 l. of pentane. After cooling to -30° for three hours the pentane solution was filtered to remove most of the crude crystalline product and was then extracted with 4% sodium hydroxide. The extract then was acidified to recover additional crude V. The pentane solution contained about 50 g. of neutral material which solidified in the ice-box but was not further investigated. The combined V was recrystallized three times from pentane to yield 562 g. (72%) of product, m. p. $69.5-71^{\circ}$; $[\alpha]^{25}_{\text{D}} -40^{\circ}$ (3.1% in 95% ethanol).

Anal. Calcd. for $\text{C}_{11}\text{H}_{17}\text{O}_2\text{Cl}$: Cl, 16.36; neut. equiv., 216.7. Found: Cl, 16.34, 16.33; neut. equiv., 216.0, 216.2.

The analysis for chlorine was made by the sodium-liquid ammonia method. After evaporation of the ammonia, the residue was dissolved in water and the solution was acidified with nitric acid. A precipitate formed which, on filtration and recrystallization from aqueous ethanol, melted at $75.2-76.2^{\circ}$. It was identified by mixing melting point comparison as 1-apocamphaneacetic acid (IX).

It was noted that the pink solution obtained from determination of the neutral equivalent clouded on warming and became colorless. Camphene was obtained as a sublimate, m. p. 46.7° , b. p. $159-160^{\circ}$ (capillary); and the lactone of 2-hydroxy-1-apocamphaneacetic acid (VII) was filtered off, recrystallized and identified by comparison with an authentic sample.² The reaction is described below for a larger batch.

2-Bromo-1-apocamphaneacetic Acid.—Twenty grams of 2-bromo-1-apocamphane- β -ethyl acetate was saponified at room temperature in about fifteen hours with a slight excess of alcoholic potassium hydroxide. Worked up in the usual manner 2-bromo-1-apocamphane- β -ethanol was obtained as a viscous brown oil which did not crystallize in the ice-box. Oxidized with chromic anhydride in acetic acid it yielded 5.9 g. (27.7% yield) of product of m. p. $75-76^{\circ}$ which on further recrystallizations from hexane and aqueous methanol melted at $77.1-77.8^{\circ}$; $[\alpha]^{25}_{\text{D}} -41.7^{\circ}$ (6% in 95% ethanol).

Anal. Calcd. for $\text{C}_{11}\text{H}_{17}\text{O}_2\text{Br}$: Br, 30.60; neut. equiv., 261.2. Found: Br, 30.15; neut. equiv., 261.8.

1-Apocamphaneacetic acid (IX) was isolated from the sodium-liquid ammonia reaction used for halogen analysis; m. p. $72-74^{\circ}$. It was identified by mixed m. p. with an authentic sample. On warming the aqueous sodium

salt resulting from the analysis for neutral equivalent, camphene (VI) and the lactone of 2-hydroxy-1-apocamphaneacetic acid (VII) were isolated and identified as above for the 2-chloro acid.

Decomposition of 2-Chloro-1-apocamphaneacetic Acid (V).—Five hundred and sixty-two grams of the acid was dissolved in a solution of 240 g. of sodium hydroxide in 2 l. of water. On warming, the solution clouded as camphene (VI) was formed. The solution was boiled gently for four hours and the camphene allowed to steam distill. The camphene was collected and dissolved in pentane.

After drying, the pentane solution was distilled, first collecting pentane at atmospheric pressure, then camphene at 100 mm. A 60×2.5 cm. Stedman column operated at 5 to 1 reflux was employed. There was collected first a forerun weighing 22.5 g., b. p. $90-91.5^{\circ}$, f. p. 48.8° ; then a series of five fractions totaling 187 g., b. p. 91.5° const., f. p. ranging from 49.2 to 49.6° ; and a residue, 14 g., of f. p. 36° . The total weight of camphene including forerun and residue was 223.5 g. (63.4% of theory). The combined constant boiling fractions showed $[\alpha]^{25}_{\text{D}} -113.5^{\circ}$ (18% in ether) and $[\alpha]^{25}_{\text{D}} -117.5^{\circ}$ (19% in toluene); $n^{25}_{\text{D}} 1.4562$; $d^{25}_4 0.8412$; M_D , calcd. 43.51, found 44.05. The physical constants are in good agreement with those of a carefully purified sample of optically inactive commercial³ camphene, f. p. 47.0° ; $n^{25}_{\text{D}} 1.4562$; $d^{25}_4 0.8410$. A mixture composed of equal weights of the *l*-camphene, f. p. 49.1° and a purified commercial camphene f. p. 47.2° possessed a f. p. of 48.1° . Simonsen⁴ reports m. p. $51-52^{\circ}$; $[\alpha]^{25}_{\text{D}} 103.89^{\circ}$, -84.9° (in ether) and states that the hydrocarbon has not been prepared optically pure. Parallel experiments starting with nopol yielded *l*-camphene of substantially identical optical purity.

The *l*-camphene was further identified by conversion to camphenilone semicarbazone, m. p. $217-218.5^{\circ}$ (uncor.), and to camphor semicarbazone, m. p. $236-238^{\circ}$ (uncor.).

The alkaline solution from which the camphene was steam distilled was acidified with 600 ml. of concentrated hydrochloric acid. An oil deposited which crystallized on several days of standing. After one recrystallization from heptane the product weighed 125 g. (26.7% yield). Two additional crystallizations from the same solvent provided an analytical sample of m. p. 199.5° and $[\alpha]^{25}_{\text{D}} -40^{\circ}$ (4.7% in carbon tetrachloride). The identity of the lactone (VII) was established by mixed m. p. with an authentic² sample of m. p. 198.6° . No m. p. depression was observed. The lactone was characterized by saponification to sodium 2-hydroxy-1-apocamphane acetate and conversion to the *p*-phenylphenacyl ester, m. p. $109.8-110.5^{\circ}$. *Anal.* Calcd. for $\text{C}_{25}\text{H}_{28}\text{O}_4$: C, 76.50; H, 7.19. Found: C, 76.1; H, 7.2.

Semicarbazone of 2-keto-1-apocamphaneacetic Acid.—The sodium salt of 2-hydroxy-1-apocamphaneacetic acid was prepared by hot saponification of the lactone (VII) (25 g.) with 75 ml. of 8% sodium hydroxide. The solution was cooled to about 15° and 276 ml. of 8% potassium permanganate was added. The mixture was allowed to stand at about 10° for three days and filtered. The manganese dioxide was washed with several 20-ml. portions of hot water. The filtrate was heated with 14 ml. of concd. hydrochloric acid for three hours at 95° , cooled to 10° and neutralized with sodium hydroxide. A trace of unreacted lactone was extracted with ether and the filtrate was then reacidified and the keto acid extracted with ether. A viscous oil, which failed to crystallize over a period of several months, was obtained on evaporation of the ether. No attempt was made to purify it. Hasselstrom and Hampton² reported their product melted at $92-93^{\circ}$; but their 2-keto acid was probably optically inactive. It was dissolved in 50 ml. of water with just enough 10% sodium hydroxide for neutralization. To the solution 13 g. of semicarbazide hydrochloride was added and the mixture heated on the water-bath for two hours. The product, filtered off and recrystallized three times from aqueous

(3) The Glidden Co., Naval Stores Division.

(4) Simonsen, "The Terpenes," Vol. II, 2nd ed., Cambridge University Press, 1949.

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 C₁₂H₁₉O₃N₃: 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*_D²⁰ 1.4818; *d*₄²⁰ 0.9633; [*α*]_D²⁰ 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 C₂₂H₂₇O₂N: N, 4.15. Found: N, 4.02.

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

Anal. Calcd. for C₁₉H₂₄O₄: 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 C₂₅H₂₈O₃: 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.

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

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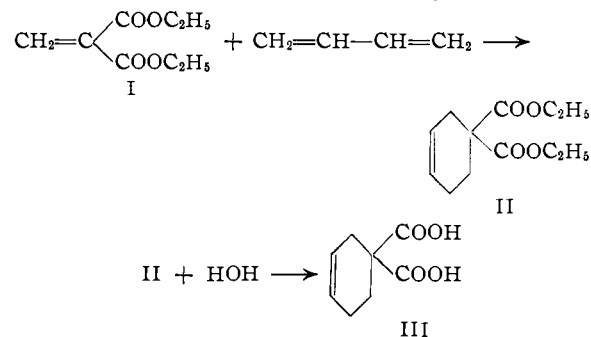
Vinylidene Cyanide. II. The Synthesis from 4,4-Dicyanocyclohexene

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The previous paper of this series¹ 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 Norton² 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 com-

pound, *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."



(1) A. E. Ardis, *et al.*, *THIS JOURNAL*, **72**, 1305 (1950).

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