Summary

1. The constituent units of lemon albedo pectin are *d*-galacturonic acid, *l*-arabinose, *d*-galactose and methyl alcohol.

2. The units are present in the approximate ratio of 4 moles of galacturonic acid to 1 mole of arabinose and 1 mole of galactose.

3. The four galacturonic acid units are chiefly present in the native pectin as methyl esters.

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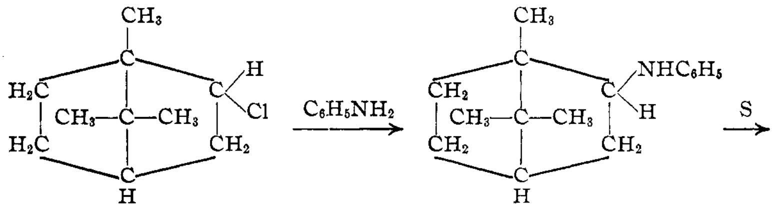
A New Camphor Synthesis

BY JOHN J. RITTER

The synthesis of camphor from α-pinene has been intensively studied because of its economic importance. Notwithstanding the voluminous literature on the subject, there appears to be only one practical method, the well-known synthesis through bornyl chloride, camphene, isobornyl acetate or formate, and isoborneol, to camphor.[1] The method suggested here was developed during the study of certain aniline derivatives of the terpenes, on which preliminary reports have already been presented before this Society.[2]

It was observed during these experiments that isobornylaniline obtained by the action of aniline on bornyl chloride[3] underwent dehydrogenation when heated with sulfur to produce camphor anil in good yield. The camphor anil so obtained is identical (with the probable exception of optical character) with the product obtained by Reddelien and Meyn[4] by condensation of aniline with camphor. Camphor anil hydrolyzes rapidly with aqueous acids to camphor and aniline. The new series of transformations is represented as follows



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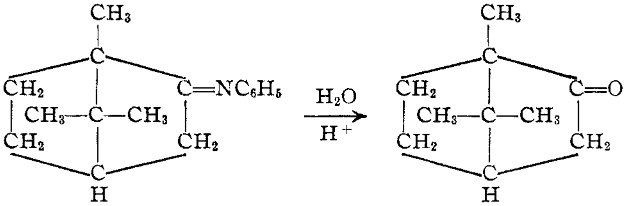
(1) The present practice in camphor manufacture is fully discussed in O. Aschan, "Die Naphthenverbindungen, Terpene, Campherarten," Walter de Gruyter, 1929, pp. 163–173.

(2) Ritter and Mottern, "The Fixation of Aniline by Hydrocarbons of the Terpene Series," American Chemical Society meeting at Buffalo, N. Y., Sept., 1931; "The Constitution of Bornylaniline," THIS JOURNAL, **54**, 3458 (1932).

(3) Ullmann and Schmidt, *Ber.*, **43**, 3202 (1910).

(4) Reddelien and Meyn, *ibid.*, **53**, 345 (1920).



The formation of isobornylaniline from bornyl chloride and aniline was first observed by Ullmann and Schmidt,[3] who assumed it to be bornylaniline, and suggested that it was an intermediate stage in the formation of camphene. It was found in this Laboratory that the same compound is formed by condensation of camphene with aniline. The latter reaction was later reported by Lipp and Stutzinger, who assigned to it the isobornyl structure.[5] These authors showed that it is formed in the Ullmann–Schmidt reaction by the addition of aniline to "primary camphene" in the presence of aniline hydrochloride. Distillation of isobornylaniline with aniline hydrochloride splits the amine completely into camphene and aniline. The reversibility of this reaction makes it evident that the system of aniline–isobornylaniline–camphene–aniline hydrochloride is an equilibrium mixture, and suggested that the low yields (45%) of isobornylaniline obtained by Ullmann and Schmidt from aniline and bornyl chloride might be made quantitative by treatment of bornyl chloride with a mixture of camphene, aniline and aniline hydrochloride in which the concentrations of the latter are so chosen as to be in equilibrium, at the end of the reaction, with a concentration of isobornylaniline equivalent to the bornyl chloride used. Experiment showed that quantitative conversion of bornyl chloride to isobornylaniline results under these conditions. This amounts, in practice, merely to continuous re-use of the same reagent, with partial neutralization after each completed cycle.

It has been found also in this work that treatment of α-pinene with aniline and aniline hydrochloride results, in part, in an amine which may be dehydrogenated to camphor anil, and is therefore bornyl or isobornylaniline. The chief product of this reaction has been found, at present, to be an isomeric amine which apparently does not belong to the bornyl or isobornyl series.

Experiments on the dehydrogenation of isobornylaniline have been confined largely to the action of sulfur. Nickel and copper have been used for the dehydrogenation of isoborneol;[6] the action of nickel on secondary amines was found by Mailhe[7] to cause splitting into olefin and primary amine. Isobornylaniline was found in the present study to behave similarly, yielding aniline and camphene when heated at 340° with

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[5] Lipp and Stutzinger, *Ber.*, **65**, 241 (1932).

[6] J. F. Houben, "Die Methoden der organischen Chemie," Geo. Thieme, Leipzig, 1925, Vol. II, p. 532.

[7] Mailhe, *Compt. rend.*, **165**, 557 (1917); **166**, 996–997 (1918).

reduced nickel. It is well known that the addition of alkalies to nickel or copper not only activates these as dehydrogenators, but serves in the case of isoborneol to prevent dehydration and formation of camphene. It is evident that the latter reaction is analogous to the elimination of aniline from isobornylaniline, and it seemed probable that the addition of alkalies might prevent this reaction. Camphene formation was found to be completely inhibited and dehydrogenation to camphor anil to occur instead under these conditions. These catalytic reactions were investigated in a preliminary fashion only, and will be the subject of further experiments. Vesterberg[8] and later Ruzicka and his co-workers[9] used sulfur successfully to dehydrogenate abietic acid and the di-cyclic sesquiterpenes. There appears to be no record of its use for the dehydrogenation of amines. In the present case, yields of 85–90% of camphor anil have been found to result in a comparatively short time.

Camphor anil is soluble in cold dilute mineral acids, but this is followed in a few minutes, even at ordinary temperature, by considerable hydrolysis. On heating to boiling, the hydrolysis is complete in a few moments. The aniline may also be recovered completely at this point.

It may be pointed out that the method outlined here has certain distinct advantages over the usual camphor synthesis. They are: (1) economy of reagents, (2) reduction of the number of operations from five to four, (3) freedom of the intermediate products, isobornylaniline and camphor anil, from hydrocarbons which render the purification of camphor difficult and (4) absence of isoborneol and camphene from the final product. The camphor obtained by this procedure has the correct melting point and cannot be distinguished by odor from natural camphor.

The study of further refinements in this method is now in progress.

Experimental Part

Isobornylaniline.—The equilibrium concentrations in the mixture of aniline, aniline hydrochloride, isobornylaniline and camphene were determined by allowing bornyl chloride to react with aniline at the boiling temperature until equilibrium was established. It was found in a series of preliminary experiments in which the initial molar ratios of bornyl chloride to aniline were 1:1.5, 1:2, 1:3 and 1:4 that, within the limits studied, increased initial ratios of aniline to bornyl chloride yields progressively increased ratios of isobornylaniline to camphene in the reaction products. The percentage conversions of bornyl chloride to isobornylaniline in the above series were 22, 34, 38 and 45, respectively, after three and one-half hours' heating. A second series with the 1:4 bornyl chloride–aniline mixture showed equilibrium to be reached after seven hours, when the percentage conversion reaches 65. Two typical procedures are outlined.

(a) Bornyl chloride (one mole, 172 g.) and aniline (four moles, 372 g.) are refluxed for seven hours. The mixture is then allowed to cool to about 100°, neutralized completely with 30% sodium hydroxide solution, and the oily layer of aniline, camphene and isobornylaniline separated. Aniline and camphene may be separated from the

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[8] Vesterberg, *Ber.*, **36**, 4200 (1903).

[9] Ruzicka and co-workers, *Helv. Chim. Acta*, **4**, 505 (1921); **5**, 345 (1922).

isobornylaniline by steam distillation (the latter is not volatile), or the oily layer may be dried and distilled under reduced pressure. Distillation up to 100° at 1 mm. removes most of the aniline and camphene. The receiver is changed when the vapor temperature reaches 130° and the isobornylaniline fraction collected. The remaining distillate consists entirely of isobornylaniline boiling at 131° at 1 mm.; weight, 148 g. To the recovered camphene and aniline there is now added bornyl chloride (0.65 mole, 112 g.), aniline hydrochloride (0.35 mole, 45.5 g.), and aniline (0.30 mole, 28 g.). On treatment of this mixture in the same manner as previously, it yields 0.65 mole of isobornylaniline (100%).

(b) One mole (172 g.) of bornyl chloride and three moles (279 g.) of aniline are refluxed for three and one-half hours. The reaction mixture separates at the end into two layers, of which the lower contains practically all of the aniline hydrochloride dissolved in a little aniline. On cooling the aniline hydrochloride crystallizes, and the supernatant layer of aniline, camphene and isobornylaniline may be decanted. This is washed with sodium hydroxide solution to ensure neutrality, dried and distilled as under (a); yield, 0.38 mole, 87 g. The recovered camphene and aniline now require 0.38 mole of aniline, 0.38 mole of bornyl chloride, and 0.62 mole of aniline hydrochloride for the next cycle, in which 0.38 mole of isobornylaniline is formed.

Camphor Anil.—Isobornylaniline (100 g.) and sulfur (14 g.) are mixed in a 200-cc. flask fitted with a short water-cooled reflux condenser connected to a trap containing 100 g. of 1:1 sodium hydroxide solution. The latter serves to show, by intermittent weighing, the progress of the reaction. The sulfur is dissolved by shaking for a few moments slightly above its melting point, and the resulting yellow solution then heated in a metal bath at 215–220°. Weighing of the trap after two hours at this temperature shows that 65% of the hydrogen sulfide has already been given off. The heating is continued for an additional two hours at 230–235°, when the amount of hydrogen sulfide reaches 85% of the calcd. The mixture is then allowed to cool somewhat and transferred to a 125-cc. Claisen flask. Distillation at 1 mm. yields 91 g., b. p. 118–135°. This is redistilled, rejecting a small quantity boiling under 115°, and the pure anil collected at 118–120°; weight, 75 g. The residue in the distilling flask is unchanged isobornylaniline; yield of camphor anil based on the amount reacting, 89.3% or about 75% of the total. Camphor anil is a pale yellow, somewhat viscous liquid with a faint but persistent garlic-like odor, characteristic also of the product from camphor and aniline.

Hydrolysis of the Anil and Isolation of Camphor.—The anil is added to a slight excess over one mole of sulfuric acid in 20% aqueous solution, and heated to boiling under a reflux for a few minutes. The camphor is then isolated by steam distillation; yield, quantitative. The steam-distilled product is filtered with suction and dried between filter papers; m. p. 173–174° (corr.).

Action of Nickel Catalysts on Isobornylaniline.—A nickel catalyst was prepared according to the directions given by Aschan.[10]

(a) Fifty grams of isobornylaniline and 5 g. of nickel are heated at 340° in a distilling flask immersed in a metal bath. No hydrogen is formed, but a mixture of aniline and camphene (18 g.) distils during five hours. This is dissolved in ether, washed successively with 10% hydrochloric acid, 10% sodium hydroxide, and water, dried over calcium chloride, and distilled at ordinary pressure after removal of the ether on the steam-bath; b. p. 160–161°; m. p. 40–41°; weight, 10 g.

(b) About 0.5 g. of potassium hydroxide is ground in a mortar with 1 g. of isobornylaniline until a uniform paste has been formed. This is transferred with the aid of the remainder of the amine (49 g.) to a 125-cc. distilling flask and 5 g. of nickel added. The flask is connected to glass tubing leading to a trough containing a receiver arranged to collect the hydrogen evolved over water. The flask is heated at 340° for two hours,

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[10] Ref. 1, p. 171.

and 1700 cc. of hydrogen collected (about 33% of the calcd.). Distillation at 1 mm. yields 11 g. of camphor anil.

Summary

A synthesis of camphor from bornyl chloride, passing through isobornylaniline and camphor anil, has been described. The yield of camphor from bornyl chloride by this procedure is 89%.

The action of nickel catalysts on isobornylaniline has been found to result, according to the conditions, in camphor anil, or a mixture of camphene and aniline.

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The Preparation of Some Mono- and Dialkylcyclohexanes

BY FRANK K. SIGNAIGO AND PAUL L. CRAMER

As a part of an investigation carried on in this Laboratory of the detonation characteristics of individual hydrocarbons,[1] many of these compounds of various types were synthesized and it was thought desirable to publish the methods used for preparing certain series of the hydrocarbons in some quantity and of a reasonably high degree of purity, and also to give certain physical constants of these compounds, several of which will be described for the first time.

This first paper describes the preparation of mono- and dialkylcyclohexanes together with that of the corresponding intermediate cyclohexanols and cyclohexenes.

The general methods which have been used for the synthesis of alkylcyclohexanes are: (1) the reaction of zinc alkyls on bromocyclohexanes,[2] (2) the hydrogenation of alkylbenzenes,[3] and (3) the addition of Grignard reagents to cyclohexanones, yielding tertiary cyclohexanols which are converted to the corresponding paraffins either (a) by the reduction of their halides[4] or (b) by their dehydration and the hydrogenation of the resulting olefins.[5] A less general method is that of Bourguel,[6] who has prepared several monoalkylcyclohexanes by the hydrogenation of acetylene hydrocarbons.

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(1) Lovell, Campbell and Boyd, *Ind. Eng. Chem.*, **23**, 26 and 555 (1931), and a paper on the detonation characteristics of naphthene hydrocarbons now in preparation.

(2) Kursanoff, *Ber.*, **32**, 2972 (1899).

(3) Sabatier and Senderens, *Compt. rend.*, **132**, 566 (1901); and others.

(4) Zelinsky, *Ber.*, **34**, 2877 (1901); **35**, 2679 (1902); Knoevenagel, *Ann.*, **297**, 159 (1897); v. Auwers, *ibid.*, **420**, 96 (1919).

(5) Murat, *Ann. chim. phys.*, [8] **16**, 119 (1909); Sabatier and Mailhe, *ibid.*, [8] **10**, 551 (1907); Mailhe and Murat, *Bull. soc. chim.*, [4] **7**, 1083 (1910); Garland and Reid, THIS JOURNAL, **47**, 2337 (1925).

(6) Bourguel, *Bull. soc. chim.*, **41**, 1475 (1927).