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* (R) signifies a paper which is chiefly concerned with a review of some aspect of the subject.

PRODUCTION OF SYNTHETIC CAMPHOR FROM INDIAN TURPENTINE

By M. L. BERI and J. L. SARIN

It is important that synthetic camphor be produced within the British Empire, if possible, in order to eliminate the usual sources of supply which are entirely of foreign origin. Exact figures of the import of camphor in the Empire countries are not available, but the value of imports of the four principal camphor importing countries, namely, United Kingdom, India, Australia, and Federated Malaya States, during the year 1933-34 were £64,471, £177,502, £10,077, and £1470 respectively.¹ The value of imports is likely to increase in future, since camphor is entering to a greater and greater extent into the perfumery, explosives, celluloid, and pharmaceutical industries. At present, natural camphor is a Japanese monopoly, while synthetic camphor is principally produced in Germany and America.

The starting material for the commercial production of synthetic camphor is turpentine of high pinene contents; both α and β pinene are useful.² In India and Burma extensive pine forests are distributed in mountainous regions. Of the five species of pine³ met in India, three are known to give a turpentine which is very high in pinene content,⁴ and should be suitable for the production of synthetic camphor. The area under pine forest is as below⁵:

Name of Province	Area under all kinds of pine trees acres	Area under pines, yielding turpentine rich in pinene		
		<i>Pinus excelsa</i> acres	<i>Pinus merkusii</i> acres	<i>Pinus khasya</i> acres
Punjab	270,000	43,300	—	—
U.P.	1,000,000	8250	—	—
Kashmir	692,000	—	—	—
N.W.F.P.	23,000	13,000	—	—
Burma	—	—	798,720	1,171,200
Southern States ...	—	—	716,800	1,267,200

Although it is not possible to work profitably for the production of turpentine the whole of these enormous

areas, nevertheless the development of this source of supply of turpentine for the manufacture of synthetic camphor undoubtedly offers an attractive proposition.

The accepted commercial process⁶ for the manufacture of synthetic camphor starts with turpentine which is fractionated to give pinene, and then goes on to bornyl chloride, camphene, isobornyl-acetate to isoborneol, and this is oxidized to camphor.⁷ The different operations of this process have been the subject of many patents and much literature.⁸ But the entire work had been carried out with American or French turpentine as the starting raw material, and there was a need for some work in connexion with the adaptation of well-known industrial processes to the Indian raw material. Accordingly, a study has been made of the most suitable reagents and conditions of reaction under which the best yield of synthetic camphor may be obtained, in carrying out the different operations of the commercial process of synthetic camphor manufacture with Indian turpentine. It may be stated that the experiments here described are purely laboratory in type and scale, and no comparable semi-commercial scale experiments have so far been carried out, consequently no deduction can be made at this stage of the work, as to the practical and economic feasibility of the manufacture of synthetic camphor from Indian turpentine.

EXPERIMENTAL

Turpentine.—Turpentine was obtained by distillation from resin of blue pine (*Pinus excelsa*)⁹. 100 parts of resin gave about 24 parts of turpentine. Turpentine was dried over sodium metal and its physical constants were determined. Sp. gr. at 17° 0.856, saponification value 3.926, (n)_D²⁰ 1.4629, (α)_D²⁰ 36.6.

Pinene.—Pinene was obtained from turpentine by fractionation with eight pears fractionating column.

100 parts of turpentine gave 94 parts of pinene. The fraction boiling between 153° to 155° C. was taken. This fraction was selected, since according to Simonsen and Rau (*loc. cit.*) it is a pure *d*-pinene.

Pinene hydrochloride.—Pinene hydrochloride was prepared from pinene by saturating pinene with thoroughly dry HCl gas, keeping the pinene well immersed in a freezing mixture. The reaction proceeds rapidly first, and is complete in 3 to 4 hours, when pinene hydrochloride separates out as a white crystalline solid. It was found that during the period of reaction the temperature should not be allowed to go above 15° C., since above this temperature no solid separates out and the liquid turns black. The solid was filtered, and the filtrate was cooled below zero, when more of the solid was found to separate out, cooling was continued until no more solid separated out. Dry HCl gas was passed once again, and any more solid obtained was filtered. The liquid remaining behind was next oxidized with dilute HNO₃ and well cooled below zero, when a further quantity of the solid separated out. Thus 73 grams of pinene hydrochloride were obtained from 100 grams of pinene, m.p. 121° to 122° C.

Camphene.—Bornyl chloride (50 g.) and potassium phenate (125 g.) were refluxed for 4 to 5 hours in a distillation flask, the side tube of which was plugged. It was then distilled and the distillate collected up to 180° C. Sodium hydroxide solution was next added to dissolve excess of phenol, if any. The oily layer of camphene was separated, dried over calcium chloride, and cooled. Yield obtained 36.5 g., m.p. 50° to 52° C., b.p. 156° to 159° C. The conversion of bornyl chloride into camphene was also tried by means of some other reagents, *e.g.*, aniline, potassium stearate, anhydrous sodium acetate, glacial acetic acid, a mixture of sodium acetate and alcoholic soda, under known conditions of reactions, but a satisfactory yield could not be obtained.

Isobornyl ester.—Camphene (30 g.), acetic acid (82.5 g.) were heated together in a flask with (2.5 g.) 50% sulphuric acid as a catalyst, for 3 to 4 hours at 50° to 60° C. The resulting mixture was poured into an empty beaker and the flask rinsed out with water, which was also transferred to the same beaker. The excess of the acid was neutralized with solid sodium carbonate and the oily layer of the ester was separated in a separating funnel, dried over calcium chloride, and then distilled under vacuum at 15 mm. pressure. Yield obtained 39.3 g., b.p. 102° to 105° C. per 15 mm.

Isoborneol.—Isobornyl acetate (26 g.) was hydrolyzed with potassium hydroxide (10 g. dissolved in 50 c.c. of alcohol) by heating it over water bath for three hours. The resulting mixture was poured in a large quantity of ice cold water. Isoborneol was precipitated, filtered, washed with water, and dried. Yield 19.5 g., m.p. 197° to 199° C.

Isoborneol to camphor.—Isoborneol (20 g.) was dissolved in nitric acid of 1.32 *d* (75 c.c.), and 50% sulphuric acid (4.8 c.c.); the mixture was heated on the water bath for about 10 hours at 80° to 90° C. with frequent shaking. The resulting product was poured with stirring over ice cold water when camphor precipitated. It was filtered out, washed with water, and then dried. Yield obtained 18.5 g., m.p. 165° to 168° C. Other oxidizing

agents such as potassium permanganate, chromic acid, nitric acid, etc. were also tried under different conditions, but satisfactory results were not obtained.

Camphene to camphor.—Camphene (15 g.) was dissolved in glacial acetic acid (50 g.) and potassium dichromate (60 g. in 150 c.c. of water), sulphuric acid of 1.84 *d* (105 g. in 150 c.c. of water) were added and refluxed at 115° to 120° C. for 18 to 20 hours and the resulting product was poured over crushed ice when camphor precipitated, which was filtered, washed with ammonia, and then with water to free it from ammonia. Yield 7.12 g., m.p. 163° to 167° C.

The action of other oxidizing agents such as potassium permanganate in acetone solution, in alkaline media, sodium perborate and sulphuric acid, nitric acid and chromic acid were tried under different conditions, but it is found that chromic acid gives the best result.

Bornyl chloride—*isobornylaniline*—*camphoranil* to *camphor*.—The method recommended by J. J. Ritter (*loc. cit.*) was followed in its details and the final yield of camphor obtained is 54% on weight of turpentine; m.p. 166° to 169° C.

Purification of camphor.—Four methods were tried to purify camphor:

- (1) Crystallization from absolute alcohol.
- (2) Camphor (crude) mixed with dilute solution of sodium hydroxide and potassium permanganate was steam distilled.
- (3) Sublimation.
- (4) Crystallization from alcohol and then subliming.

It was found that camphor purified by methods Nos. 3 and 4 above was the purest; m.p. 171° to 172° C.

SUMMARY

A study has been made of the conditions under which well-known methods of manufacture of synthetic camphor may be adapted to Indian turpentine. Information has been supplied about the most suitable reagents and conditions of reaction for the different operations of the process. The yield of camphor obtained from Indian turpentine by experiments on a laboratory scale is 54% on the weight of turpentine which is higher than that obtained so far from American turpentine.¹⁰ It appears possible that with experiments on a semi-commercial scale better yield may be obtained. It has been shown that a source of supply of the raw material for the manufacture of synthetic camphor exists within the Empire.

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⁹ The blue pine resin was supplied by the Assistant Conservator of Forests, Rawalpindi (North Punjab).

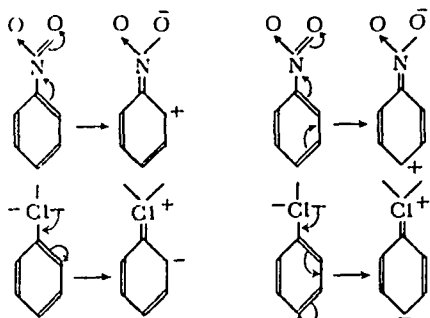
¹⁰ Acharya and Wheeler (*loc. cit.*).

A NEW RULE FOR SUBSTITUTION IN THE BENZENE NUCLEUS

By J. C. McGOWAN

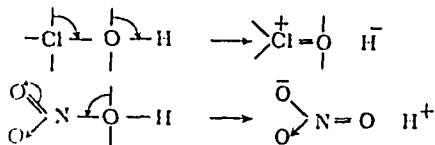
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The applications of the electronic theory of valency to substitution in aromatic nuclei are now well known.¹ Electromeric effects, when carried to completion, give structures contributing to the resonance formula. These effects are shown below in the cases of nitrobenzene, giving meta-substitution, and chlorobenzene, giving ortho- and para-substitution (always towards kationoid reagents).



The part of the electromeric effects occurring in the normal molecule is generally called the "mesomeric effect" and substitution is governed by this. L. E. Sutton² considers the difference in the dipole moments of the phenyl and corresponding tertiary butyl compounds gives a measure of this mesomeric effect.

The object of this paper is to suggest another method for the comparison of mesomeric effects. The effect of a chlorine atom or nitro group, when attached to a hydroxyl instead of a phenyl group, may be to give the following tendencies:



The nitro group would thus assist, while the chlorine atom would resist, the dissociation of the hydrogen as a proton. Some relationship might therefore be expected between the dissociation constant $K = \frac{[AO^-][H^+]}{[AOH]}$ for the compound AOH and the directive influence of the group or atom A— in A—. Strong evidence in favour of this view is shown in the table³ on p. 608.

The value of K for H₂SO₃ in the table is actually $\frac{[H^+][HSO_3^-]}{[H_2SO_3] + [SO_2]}$ which must therefore be smaller than the true K and in some other cases (*e.g.*, HCO₃⁻) the values of K may be unreliable. Further, it is not possible to obtain K for all the compounds AOH corresponding to the phenyl derivatives A—: for example —CH₂COOH and —CCl₃.

From the facts considered in this paper the following new rule is put forward:

Substitution in the compound A— by kationoid reagents will give largely ortho and para derivatives if the dissociation constant $K = \frac{[AO^-][H^+]}{[AOH]}$ of the compound AOH (measured in dilute aqueous solution at room temperature) is smaller than 10⁻⁷ and will give largely the meta derivative if K is greater than 10⁻⁵ gram mols. per litre.

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NICKEL INDUSTRY IN CANADA

The International Nickel Co. of Canada, Ltd., which in 1929 completed a programme of mine development and plant construction, involving an outlay of \$50,000,000, is expending \$12,000,000 this year in the construction of new plants, and in additions to facilities of existing plants. In the Sudbury area, in Ontario, where its mines are located, the company's programme includes the erection of a new smelter, and a new change house, and additions to its concentrator. The new smelter is to handle copper feed only, while the present smelter will operate entirely on nickel ores. The concentrator capacity is being enlarged to 12,000 tons of ore daily, as against the present capacity of 8000 t. daily. At Port Colborne, Ontario, the nickel refinery is being enlarged to produce 12,000,000 lb. of electrolytic nickel a month, an increase of 50% over the present capacity; and at Clydach, Wales, additions are being made to the refining facilities, which will enable an annual production of 42,000,000 lb. of metallic nickel.

Falconbridge Nickel Mines, Ltd. is expanding its plant facilities both in the Sudbury area, and in Norway, to enable a 25% increase in the company's productive capacity. Plans are under way also for the production of various nickel alloys in the electrolytic furnace at Orillia, Ontario. The enlarged plant in the Sudbury area is expected to be in full operation by the end of 1936, and will enable the company to treat close to 400,000 tons of ore annually as compared with the present rate of 300,000 tons annually.