73. *The Isolation of Indene from Heavy Naphthas.*

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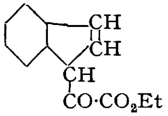
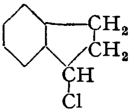
Two new methods, based on the formation of ethyl indenyl-1-glyoxylate and 1-chlorohydrindene respectively, have been developed for the recovery of high-quality indene from commercial naphthas.

Published methods for the isolation of indene from heavy naphtha fractions include (*a*) crystallisation of the picrate and subsequent decomposition with steam (Krämer and Spilker, *Ber.*, 1890, **23**, 3276), (*b*) formation of sodioindene by means of sodamide, followed by steam decomposition (Weissgerber, *Ber.*, 1909, **42**, 569; D.R.-PP. 205,465, 209,694), (*c*) azeotropic distillation (U.S.PP. 2,279,778, 2,279,779, 2,279,780). Each of these has certain disadvantages and the two new methods now reported may prove more economical and convenient.

Condensation of indene with ethyl oxalate in alcoholic solution in the presence of sodium ethoxide (Wislicenus, *Ber.*, 1900, **33**, 773; Thiele, *ibid.*, p. 851) yields ethyl indenyl-1-glyoxylate, (I) m. p. 89—90°, which may be removed from the heavy naphtha residue by utilising its solubility in sodium hydroxide solution. Optimum conditions for the recovery of the indene from the sodio-derivative of (I) have been examined, and unless very pure indene is desired, it is unnecessary, and indeed unprofitable, to isolate the ester (I) from the reaction mixture.

(I.)





(II.)

Indene absorbs hydrogen chloride with the formation of 1-chlorohydrindene (II) (Weissgerber and Brehme, *Ber.*, 1911, **44**, 1436; Courtot and Dordelinger, *Compt. rend.*, 1924, **179**, 1168) which boils some 30° higher than indene, and forms the basis of the second method for the separation of pure indene from commercial naphthas.

Experimental.

*Ethyl Indenyl-*1*-glyoxalate* (I).—Steam-distilled and dried indene (10 g., s. p. — 1·8°) was added with shaking and water-cooling to a solution of ethyl oxalate (12 g.) in absolute alcohol (40 c.c.) in which sodium (2 g.) had been dissolved. After 0·25 hour, the orange-coloured solution was poured into water (500 c.c.), neutral matter removed in ether, and the aqueous layer acidified with concentrated hydrochloric acid. The orange-yellow precipitate was extracted with ether, the extract dried, and the solvent removed. The residue crystallised from benzene in orange-yellow rhombs (8·4 g.), m. p. 89—90°, unchanged by further recrystallisations from the same solvent (Wislicenus, *loc. cit.*, gives m. p. *ca.* 80°).

Recovery of Indene from the Above Ester.—The ester (I) (20 g.) was dissolved in 20% sodium hydroxide (120 c.c., *ca.* 6 mols.) and after 3 hours at room temperature the solution was distilled in steam for 2—3 hours. The distillate was extracted with ether, the extract dried, and the solvent removed through a short column. Distillation of the residue gave indene (7·5 g.), b. p. 74—75°/16 mm., s. p. — 1·7°.

Recovery of Indene from Heavy Naphtha by Ethyl Oxalate Method.—The following represents a typical experiment. Steam-distilled and dried heavy naphtha (14·4 c.c. containing 69% of indene, estimated by the method of Weger and Bilman, *Ber.*, 1903, **36**, 640) was added with shaking and cooling to a solution of ethyl oxalate (12·4 g.) in ethyl alcohol (40 c.c.) containing sodium (2·0 g.). After 0·25 hour, water was added, neutral impurities removed in ether,* and solid sodium hydroxide (110 g.) added with cooling to the aqueous layer (450 c.c.). After 3 hours at room temperature the solution was steam-distilled, and the indene (6·8 g.), b. p. 72—74°/17 mm., s. p. — 2·20°, was isolated from the distillate by ether extraction.

When the indene content of the heavy naphtha is low (*e.g.*, 10—50%) the inert alkali-insoluble oil can be separated and the ether extraction at this stage becomes unnecessary.

The results from a selection of experiments included in Table I indicate that indene of high purity can be obtained in 65% yield from heavy naphtha fractions originally containing 10—100% of indene.

Recovery of Indene from Heavy Naphtha by Hydrogen Chloride Method.—Naphtha (100 g., washed with alkali and acid) was saturated with dry hydrogen chloride at — 5° to — 10° (not critical), and after 3 hours, excess was removed in a stream of air. The residue was fractionated at 2 mm. (12 mm. has also been used) from an oil-bath, a glass spiral column 7″ long being used. The batch was kept at 95° until most of the non-indene fraction, b. p. 55—79°/2 mm., which may be profitably refractionated, was obtained. Distillation of the residue yielded 1-chlorohydrindene, b. p. 79—81°/2 mm., but this operation was usually omitted and the total residual oil was refluxed with anhydrous sodium carbonate (0·7 part) for 0·7 hour, in an oil-bath at 160—170°. The indene was recovered by steam distillation, dried, and distilled.

The copious evolution of hydrogen chloride observed on warming 1-chlorohydrindene with sodium carbonate suggests that decomposition occurs in the vapour phase, but some basic substance must be

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* Unless the naphtha was subjected to a preliminary steam-distillation, which removed traces of polymeric and oxidation products, objectionable emulsions were obtained at this stage.

TABLE I.

Recovery of indene from heavy naphthas.

Source of indene.	S. p.	Purity, %.	S. p. of indene recovered.	Purity, %, of indene recovered.	Recovery, %.
1. Special close-up naphtha fraction from Dorman Long & Co.; b. p. 180—182°	−17·7°	69	−2·2°	97·5	68
2. Dorman Long & Co.'s naphtha; b. p. 175—182°	−26·0	55	−2·4	97·0	67
3. Synthetic mixture containing pure indene and indene-free naphtha	—	11	−3·3	96·0	67

present in order to inhibit the acid-catalysed liquid-phase polymerisation of the indene. Experiments with sodium hydroxide, lime, pyridine, and diethanolamine instead of sodium carbonate have given inferior results.

Typical results with five naphtha samples (each 100 g.) given in Table II show that this method is satisfactory in the case of heavy naphthas supplied by Dorman Long and Co. and the Consett Iron Co., but that it fails with certain naphthas. The failures were first thought to be due to the presence of coumarone in the naphtha, but it was shown that, although this compound absorbs dry hydrogen chloride, yet the gas is completely eliminated by air aspiration. It is probable that the failures are due to the presence of unidentified, unsaturated compounds which combine with hydrogen chloride to form addition compounds inseparable from 1-chlorohydrindene by distillation.

TABLE II.

Source of naphtha.	Purity, %.	Yield of residual oil (A), %.	Yield of recovered indene, %.	S. p. of recovered indene.	Purity, %, of recovered indene.	Recovery of indene, %.
a. Dorman Long & Co.	66	90·8	49·2	− 2·6°	98·5	73
a'. ,, ,, ,, ...	66	84·3	47·9	− 2·5	99	72
b. ,, ,, ,, ...	55	64·4	39·7	− 4·0	96	69
b'. ,, ,, ,, ...	55	69·7	38·3	− 4·1	96	67
c. Consett Iron Co.	38	50·5	27·3	− 3·3	97	70
d. Gas Light & Coke Co.	27	24·0	12·7	−14·5	76	36
d'. ,, ,, ,, ...	27	20·0	11·0	−13·6	78	31
e. Birchenwood Coal & Coke Co.	17	30·0	17·6	−11·0	83	86

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