8. *A New Synthesis of Cadalene.*

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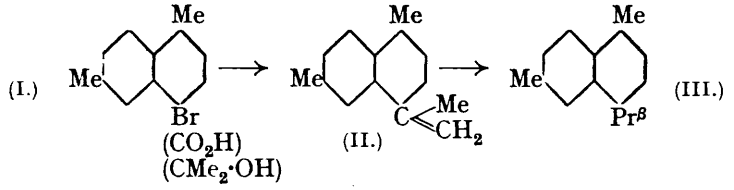
THE constitution assigned to cadalene (1 : 6-dimethyl-4-*iso*propylnaphthalene) is based chiefly on its synthesis from carvone by Ruzicka and Seidel (*Helv. Chim. Acta*, 1922, **5**, 369). An element of uncertainty is introduced by the use of aluminium chloride to effect ring-closure, for migrations of alkyl groups are frequently encountered under the influence of this reagent. The importance of cadalene as a product of dehydrogenation of a large group of sesquiterpenes led us to seek confirmation of its structure by a simpler synthesis from 1 : 6-dimethylnaphthalene. This is a constituent of coal tar which is now available in quantity, and its constitution is beyond dispute.

Weissgerber and Kruber (*Ber.*, 1919, **52**, 348) showed that sulphonation of 1 : 6-dimethylnaphthalene occurs in position **4**, and one of us (Cook, J., 1931, 489) has found that acid chlorides also condense in this position. It was therefore reasonably certain that

bromination in the dark, in a solvent, would lead to 4-*bromo*-1 : 6-*dimethylnaphthalene* (I). This bromo-compound was converted through the medium of its magnesium derivative into 1 : 6-*dimethyl*-4-*naphthoic acid*; the *dimethylcarbinol* arising from the interaction of the *ethyl* ester of this acid and methylmagnesium iodide was dehydrated by picric acid in alcoholic solution, and gave the *picrate* of 1 : 6-*dimethyl*-4-iso*propenylnaphthalene* (II) :



Reduction of the ethylenic hydrocarbon was best effected by sodium and alcohol; this also resulted in partial hydrogenation of the naphthalene ring; the product was therefore finally dehydrogenated with selenium, and the dimethyl*iso*propylnaphthalene thus formed was identical with cadalene.

An attempt to simplify this procedure by direct reduction of the carbinol (I) with hydriodic acid in boiling acetic acid led almost exclusively to dimerisation of the ethylenic hydrocarbon (II); there was also formed a small amount of cadalene, the isolation of which is of importance, as it precludes the possibility of molecular rearrangement having been effected by the high temperature necessary for the above-mentioned selenium dehydrogenation.

The facile dimerisation of 1 : 6-dimethyl-4-*iso*propenylnaphthalene is of interest, and it seems clear that the *p*-methyl group assists the process, for the reaction is brought about by hydrochloric acid in boiling acetic acid, whereas 1-*iso*propenylnaphthalene was not converted into its saturated dimeride by this means, although sulphuric acid in boiling acetic acid effected the change (Cook, J., 1932, 466). The facilitating influence of the *p*-methyl group in promoting dimerisation was doubtless also responsible for the failure to obtain 1-methyl-4-*iso*propylnaphthalene by hydriodic acid reduction of the corresponding *iso*propenyl compound, although in this case the pure dimeride was not isolated.

The *apo*cadalene obtained by Ruzicka and Mingazzini (*Helv. Chim. Acta*, 1922, **5**, 710) by elimination of a methyl group from cadalene was assumed to be 3-methyl-5-*iso*propylnaphthalene, as it was not identical with 1-methyl-4-*iso*propylnaphthalene, which these authors prepared by a method also involving the use of aluminium chloride. We have now obtained 1-methyl-4-*iso*propylnaphthalene much more simply from the ethyl ester of 1-methyl-4-naphthoic acid, by treatment with methylmagnesium iodide, and subsequent dehydration and reduction.

Experimental.

4-*Bromo*-1 : 6-*dimethylnaphthalene* (I).—A mixture of pure 1 : 6-dimethylnaphthalene (supplied by the Gesellschaft für Teerverwertung: picrate, m. p. 111—112°; lit., 114°) (156 g.) and CS_2 (350 c.c.) was treated slowly with Br (50 c.c.), and then warmed on the water-bath. After removal of the solvent, the residue was twice distilled in vac., yielding 125 g. of a const.-boiling fraction. A sample for analysis was agitated with warm KOH in MeOH and twice distilled in vac.; it was then a very pale yellow, mobile liquid, b. p. 171—172°/15 mm. (Found: C, 61·8; H, 4·85. $C_{12}H_{11}Br$ requires C, 61·3; H, 4·7%). The *picrate* separated from EtOH in orange needles, m. p. 114° (Found: C, 46·8; H, 3·7. $C_{12}H_{11}Br,C_6H_3O_7N_3$ requires C, 46·6; H, 3·0%).

1 : 6-*Dimethyl*-4-*naphthoic Acid* (I).—A slow stream of CO_2 was led into an ice-cold Grignard solution prepared from the aforesaid bromo-compound (100 g.) and Mg turnings (10 g.) in anhyd. Et_2O (500 c.c.). After 6 hr. the solution was allowed to warm to room temp., passage of CO_2 being continued for a further 12 hr. The acidic product was isolated by known methods and recrystallised from AcOH and then xylene (yield, 20 g.; m. p. 185—188°). Colourless needles of pure 1 : 6-*dimethyl*-4-*naphthoic acid*, m. p. 188—189°, were obtained by recrystn. from C_6H_6 (Found: C, 77·85; H, 5·9. $C_{13}H_{12}O_2$ requires C, 78·0; H, 6·05%).

The *ethyl* ester was formed by heating the acid (67 g.) under reflux for 5 hr. with EtOH saturated with HCl (150 c.c.) diluted with EtOH (300 c.c.). The ester (66 g.) formed a colourless

viscous liquid, b. p. 166°/3—5 mm., which crystallised after several weeks (Found: C, 79·0; H, 7·1. $C_{15}H_{16}O_3$ requires C, 78·9; H, 7·1%).

1 : 6-*Dimethyl*-4-iso*propenylnaphthalene* (II).—An ethereal solution of the above ester (23 g.) was added to a Grignard solution prepared from MeI (16 c.c.) and Mg turnings (6 g.), cooled in a freezing mixture. After addition of the ester, the solution was allowed to warm to room temp., then boiled for 1 hr., and decomposed with ice and NH_4Cl. The Et_2O was removed from the washed and dried solution on the water-bath. The residual *carbinol* (I), a gum which could not be obtained cryst., was heated on the water-bath for 2½ hr. with picric acid (24 g.) in EtOH (350 c.c.). On cooling, the *picrate* of 1 : 6-*dimethyl*-4-iso*propenylnaphthalene* (II) separated as orange-red needles (21 g.), m. p. 118—119° after recrystn. from EtOH (Found: N, 10·0. $C_{15}H_{16},C_6H_3O_7N_3$ requires N, 9·9%). *Dehydrocadalene* (II), isolated from the picrate, formed a colourless mobile liquid, b. p. 154°/14 mm. (Found: C, 91·9; H, 8·2. $C_{15}H_{16}$ requires C, 91·8; H, 8·2%).

1 : 6-*Dimethyl*-4-iso*propylnaphthalene* (III).—A solution of dehydrocadalene (5 g.) in boiling EtOH (50 c.c.) was treated gradually with Na (4 g.). The reduction product was distilled in vac. and dehydrogenated with Se (4 g.) at 300—320° for 22 hr. The product was treated with picric acid (4·5 g.) in EtOH, the resulting picrate decomposed with Na_2CO_3, and the hydrocarbon distilled in vac. over Na; b. p. 153—154°/15 mm.; yield, 2 g. The 1 : 6-dimethyl-4-*iso*propylnaphthalene so obtained gave a picrate, m. p. 114—115° (alone or mixed with authentic cadalene picrate), and a styphnate, m. p. 140° (Ruzicka and Seidel, *loc. cit.*, give 139° for cadalene styphnate).

Dimeride of Dehydrocadalene.—A solution in AcOH (300 c.c.) of the crude carbinol from 23 g. of 1 : 6-dimethyl-4-naphthoic ester was boiled for 2 hr. with HI (*d* 1·9; 40 c.c.). The colourless cryst. solid which separated (12 g.) was in every way analogous to the dimeride of 1-*iso*propenylnaphthalene (Cook, J., 1932, 466), and after crystn. from C_6H_6 had m. p. 218° (Found: C, 91·8; H, 8·3. $C_{30}H_{32}$ requires C, 91·8; H, 8·2%). This compound was also obtained when a solution of dehydrocadalene (II) in AcOH containing HCl was boiled for 2 hr.

The AcOH liquors from the HI reduction were diluted with H_2O and extracted with Et_2O. After removal of the Et_2O the residual oil was treated with ice-cold conc. H_2SO_4 to remove olefin, and the unattacked oil distilled in vac. The product (0·5 g.) gave a picrate which after 2 recrystns. from EtOH had m. p. 112—113°, not depressed by cadalene picrate.

Dimethyl-(4-methyl-1-naphthyl)carbinol.—This was prepared from ethyl 4-methyl-1-naphthoate (Mayer and Sieglitz, *Ber.*, 1922, **55**, 1839) (10·7 g.) and MeMgI (from 7 c.c. MeI and 2·5 g. Mg turnings) exactly as described above for the dimethylnaphthoic ester. The crude liquid *carbinol* became solid under light petroleum and after several recrystns. from C_6H_{12} formed colourless fibrous needles, m. p. 90° (not sharp) (Found: C, 84·0; H, 8·4. $C_{14}H_{16}O$ requires C, 84·0; H, 8·0%). The indefinite m. p. was probably due to contamination with a pinacol reduction product of an intermediate ketone; no improvement resulted from the use of a larger excess of a filtered solution of MeMgI.

When this carbinol was reduced with HI in boiling AcOH no pure compound could be isolated.

1-*Methyl*-4-iso*propenylnaphthalene.*—A solution of the foregoing carbinol (12 g.) in EtOH (60 c.c.) and conc. HCl (2·5 c.c.) was heated on the water-bath for 1 hr. After dilution with H_2O the product was extracted with Et_2O and distilled in vac. The const.-boiling olefin (9·5 g.) gave a *picrate*, which crystallised from EtOH in orange needles, m. p. 88° (Found: C, 58·0; H, 4·6. $C_{14}H_{14},C_6H_3O_7N_3$ requires C, 58·4; H, 4·2%). The same picrate was also obtained by heating the carbinol with alc. picric acid.

1-*Methyl*-4-iso*propylnaphthalene.*—1-Methyl-4-*iso*propenylnaphthalene (8·9 g.) was reduced with Na (7 g.) in boiling EtOH (100 c.c.), and the product dehydrogenated by Se (8 g.) at 280—300° for 20 hr. The resulting *apo*cadalene was distilled in vac. over Na (yield, 5·8 g.): it was then purified through the picrate and redistilled; b. p. 148°/16 mm. (Found: C, 91·2; H, 8·9. Calc. for $C_{14}H_{16}$: C, 91·3; H, 8·7%). The picrate of this 1-methyl-4-*iso*propylnaphthalene formed orange needles, m. p. 100—101° (Ruzicka and Mingazzini, *loc. cit.*, give 99—100°). A sharp-melting styphnate could not be obtained.

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