I. SOME REACTIONS OF CARONE.

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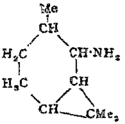
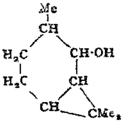
In a recent communication (*Journ. Chem. Soc.*, 1926, 2049) experiments were described which had as their object the preparation of the secondary alcohol (II) for which the name *carol* is suggested. It was found that when carone was catalytically hydrogenated it behaved like an αβ-unsaturated ketone, fission of the *cyclo*propane ring taking place with formation of monocyclic derivatives. We decided to attempt the preparation of the alcohol by the action of nitrous acid on carylamine (I). *d*-Carylamine was prepared by Baeyer (*Ber.*, 1894, **27**, 3485) by the reduction of *d*-caroneoxime with alcohol and sodium, the base, which was not isolated in a pure state, being characterised by the preparation of derivatives. Although the hydrochloride of the base is unstable and passes readily into the monocyclic unsaturated base, vestrylamine, we have found no difficulty in obtaining *d*-carylamine in considerable quantity as a mobile oil b.p. 86–89°/15 mm. When the sulphate is treated with nitrous acid it is readily converted into l-*carol* (II) although the yield is poor. The alcohol is laevorotatory and is undoubtedly bicyclic since it is comparatively stable to an alkaline solution of potassium permanganate and on oxidation with chromic acid yields carone. The alcohol has a remarkably high molecular refraction $[R_L]_D$ 46.78 ; calc. 46.2) and we cannot offer any explanation of this abnormality.


I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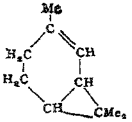
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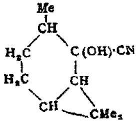
IV

It was of interest to attempt the elimination of water from carol since if this proceeded normally it should yield Δ^4-carene (III). Owing to the marked instability of the bicyclic structure the reagents available for this reaction were somewhat limited; we have only examined the action of the Grignard reagent on the alcohol and the decomposition of its methyl xanthogenate.

When *l*-carol is treated with a large excess of the Grignard reagent elimination of water takes place but the reaction proceeds apparently in a complex manner since the hydrocarbon obtained distils over a wide range. A consideration of the physical constants of the oil and an examination of its reaction with bromine lead us to the conclusion that the mixture consists essentially of monocyclic terpenes. On treatment with hydrogen chloride a small quantity of a crystalline hydrochloride was obtained which was identified as terpinene dihydrochloride. The amount of terpinene present in the hydrocarbon mixture cannot however be large since we were unable to prepare the characteristic nitrosate nor could αγ-dihydroxy-α-methyl-δ-*iso*propyladipic acid be separated from the acids formed on oxidation with potassium permanganate. We were not able to identify the other terpenes present, but no evidence could be obtained of the presence of either dipentene or sylvestrene.

When the sodium derivative of *l*-carol is treated with carbon bisulphide followed by methyl iodide, *methyl carylxanthogenate* is obtained as a viscid oil which shows no tendency to crystallise. On distillation at the ordinary pressure the xanthogenate is decomposed with formation of a hydrocarbon which after repeated distillation over sodium boils at 165–170°/685 mm. This hydrocarbon has constants agreeing very closely with those of Δ^4-carene as will be seen from the following comparative table.

	d-Δ^4-*Carene*	*Synthetic Hydrocarbon*
b.p.	165·5–167°/707 mm.	165–170°/685 mm.
$d_{30°}^{30°}$	0·8552	0·8551
$n_D^{30°}$	1·474	1·473
$[\alpha]_D$	62·2°	–5·96° (in acetic acid)

When available only in small quantity Δ^4-carene is not readily identified, since it does not yield any crystalline derivatives and it can only be characterised by conversion into sylvestrene dihydrochloride or by oxidation to 1 : 1-dimethyl-2-γ-keto*cyclo*propane-3-carboxylic acid. The quantity (2 g.) of synthetic hydrocarbon was insufficient for oxidation and we therefore treated an acetic acid solution with hydrogen chloride. The resulting product was an oil which, when cooled in a mixture of solid carbon dioxide and acetone crystallised, but melted below –15°. In view of the low rotation of the hydrocarbon the products of the reaction, assuming it to have been Δ^4-carene would consist of carvestrene and dipentene dihydrochlorides, a mixture which would undoubtedly have a very low melting point. We do not therefore consider that the result of this experiment can be regarded as definite evidence that the terpene was not Δ^4-carene. The yield of the hydrocarbon by this method of synthesis is however so extremely poor that we are not at present in a position to repeat its preparation.

It was mentioned above that on reduction carone behaved like an $\alpha\beta$-unsaturated ketone, and it appeared to us of interest to examine its reactions with hydrogen cyanide and ethyl sodiocyanoacetate. With hydrogen cyanide carone behaves like a saturated ketone yielding the corresponding *cyanhydrin* (IV). Attempts to hydrolyse this to the hydroxy-acid by means of alkali were unsuccessful, hydrogen cyanide being eliminated with regeneration of the ketone. This result was not unexpected in view of the previous work of Lapworth (*Journ. Chem. Soc.*, 1910, **97**, 12) and Auwers and Krollpfeiler (*Ber.*, 1915, **48**, 1389). With ethyl sodiocyanacetate carone shows no tendency to react although the experiment was made under various conditions.

EXPERIMENTAL.

d-*Carylamine.*

d-Carylamine was prepared by the reduction of caroneoxime as described by Baeyer (*loc. cit.*). It was a colourless mobile oil possessing a somewhat characteristic basic smell; b.p. 86–89°/15 mm., in 2·8 per cent. alcoholic solution $[\alpha]_{D}^{24°}$ 72·3° (Found: N, 9·5; $C_{10}H_{19}N$ requires N, 9·2 per cent.).

l-*Carol.*

To sulphuric acid (32·2 cc.; 9·62 per cent.) which was well cooled in a freezing mixture and mechanically stirred, *d*-carylamine (5 g.) was slowly added, care being taken that the temperature did not rise above 0°. When the addition was complete a solution of barium nitrite (7·5 g.) was added, the temperature being maintained between 5° and 10°. A brisk evolution of nitrogen was observed and the stirring was continued until this ceased (about 8 hours). When the reaction was complete the solution was basified and distilled in steam, the aqueous distillate saturated with ammonium sulphate and repeatedly extracted with ether. The combined ethereal extract was washed with dilute sulphuric acid (10 per cent.) to remove any unchanged base, then with dilute sodium carbonate solution, dried and evaporated. The oil which remained (30 per cent.) had b.p. 141–142°/100 mm. *l*-Carol is a colourless oil with a pleasant smell reminiscent of linalol; in alkaline solution it only very slowly decolorises a solution of potassium permanganate. The following constants were observed:—$d_{30°}^{30°}$ 0·9181, $n_{d}^{30°}$ 1·472; $[\alpha]_{D}^{26°}$ −42·92°; $[R_L]_D$ 46·78 (Found: C, 77·8; H, 11·9; $C_{10}H_{18}O$ requires C, 77·9; H, 11·7 per cent.).

When the alcohol was dissolved in acetic acid and the solution treated with the calculated quantity of chromic acid, it was slowly oxidised to carone which was identified by the preparation of the semicarbazone.

Action of magnesium methyl iodide on l-*Carol.*

l-Carol (50 g.) dissolved in twice its volume of ether was added gradually to a well-cooled solution of the Grignard reagent prepared from 30 grams of magnesium. The reaction was vigorous, and after three days at the room-temperature ice was added and sufficient hydrochloric acid to decompose the magnesium salts. On removal of the solvent an oil remained which on distillation was separated into two main fractions (i) b.p. 172–174°/683 mm.; $d_{30^\circ}^{30^\circ}$ 0·8392; $n_{\mathrm{d}}^{30^\circ}$ 1·4678, $[\alpha]_{\mathrm{D}}^{26^\circ}$–46·52°, $[\mathrm{R_L}]_{\mathrm{D}}$ 45·07; (ii) b.p. 180–190°/683 mm.: $d_{30^\circ}^{30^\circ}$ 0·8624, $n_{\mathrm{D}}^{30^\circ}$ 1·4745, $[\alpha]_{\mathrm{D}}^{26^\circ}$–58·48°, $[\mathrm{R_L}]_{\mathrm{D}}$ 44·42. Titration with bromine indicated that both fractions consisted essentially of monocyclic hydrocarbons containing two ethylene linkages. On treatment with hydrogen chloride in acetic acid solution an oil was obtained which on cooling in ice deposited a small quantity of a crystalline solid, m.p. 51–52°. This was identified as terpinene dihydrochloride by the method of mixed melting point. The yield of dihydrochloride was small and the oil did not yield terpinene nitrosite, whilst the product of oxidation with an alkaline solution of potassium permanganate was a viscid oil which could not be induced to crystallise.

l-*Methyl carylxanthogenate.*

l-Carol (22 g.) was added to finely divided sodium (5 g.) suspended in toluene (75 g.) and the mixture heated to boiling for 20 hours. The toluene solution of the sodium derivative was decanted from unchanged sodium and after the addition of ether (100 cc.) the well-cooled mixture was gradually treated with carbon bisulphide (25 g.). To the xanthogenate prepared in this manner methyl iodide (20 g.) was added and the conversion into the methyl ester completed by digestion on the water bath for one hour. The reaction product was poured into water, the toluene-ether separated and the solvents removed under diminished pressure. l-*Methyl carylxanthogenate* was a viscid yellow oil which did not crystallise. On distillation at the ordinary pressure an oil was obtained containing considerable quantities of sulphur compounds. It was purified by repeated distillation over sodium when it had b.p. 165–170°/685 mm. and the constants given on p. 2 (Yield 3 g.) When dissolved in acetic anhydride and treated with a drop of sulphuric acid a purple colour developed which on keeping gradually changed to red. The action of hydrogen chloride has already been discussed.

d-*Caronecyanhydrin.*

To a freshly prepared solution of hydrogen cyanide (2 g.) in alcohol (20 cc.) *d*-carone (10 g.) in alcohol (10 cc.) was added. After remaining overnight an aqueous solution of potassium cyanide (4 g. in 10 cc.) was added and the mixture digested on the water bath for three hours. The oil which separated on addition of water was extracted with ether, the ethereal extract washed with dilute alkali and the solvent removed. The crude cyanhydrin still contained much unchanged ketone and the treatment with hydrogen cyanide was repeated when the nearly pure *cyanhydrin* was ultimately obtained as a viscid oil (Found: N, 7·1; $C_{11}H_{17}ON$ requires N, 7·8 per cent.). When the cyanhydrin was digested with an aqueous solution of potassium hydroxide, ammonia was evolved and *d*-carone regenerated, the yield being quantitative.