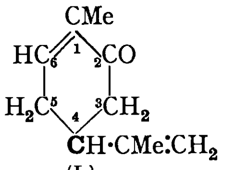
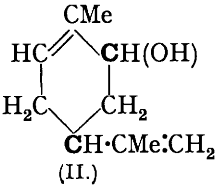
61. *Researches in the Carvone Series. Part II. Some Unsaturated Alcohols.*

By ROBERT G. JOHNSTON and JOHN READ.

THIS paper deals mainly with new work on carveols (II) and dihydrocarveols (III), all of which were prepared from carvone (I) :


(I.)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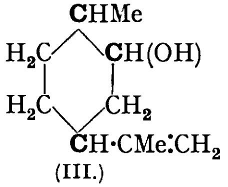
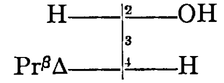

(III.)

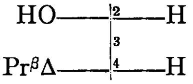
The number of dissimilar asymmetric carbon atoms (shown in Clarendon type) in these systems ranges from one to three. In conducting stereochemical studies in this group, we have sought in general to start with the simpler systems, and to introduce only one new asymmetric centre at a time : in such cases, a pure optically active compound gives rise to only two new substances. Separation has then been effected sometimes by fractionally crystallising the 3 : 5-dinitrobenzoates or the *p*-nitrobenzoates, and sometimes by taking advantage of the different rates of reaction of the corresponding acid chlorides with the stereoisomeric alcohols. These esters crystallise well, and are eminently suitable for the purpose in view.

Two pairs of optically active carveols should exist, but hitherto no pure optically active carveol has been isolated (cf. Genvresse, *Compt. rend.*, 1901, **132**, 414; Blumann and Zeitschel, *Ber.*, 1914, **47**, 2673). The most important work on the preparation of these substances is that of Ponndorf (*Z. angew. Chem.*, 1926, **39**, 138), who obtained an optically active specimen of carveol by the reducing action of aluminium *iso*propoxide on *d*-carvone dissolved in dry *iso*propyl alcohol. This reaction affords a valuable method of reducing unsaturated ketones to the corresponding unsaturated secondary alcohols, and has been used repeatedly in the present researches. We show below that the crude product obtained from *d*-carvone, and having $\alpha_D^{16^\circ}$ from + 100·9° to + 108·2°, is separable by means of the

3 : 5-*dinitrobenzoate* into two stereoisomerides, d-trans-*carveol* and d-cis-*carveol*, having $[\alpha]_D^{25^\circ}$ + 213·1° and + 23·9°, respectively; the first of these is liquid, the second solid, at the ordinary temperature. The liquid alcohol, because of its lower density and refractive index (see table below), would appear, in accordance with the Auwers–Skita rule (cf. *Ber.*, 1926, **59**, 2299), to possess the *trans*-configuration (IV):



(IV.) *d*(or *l*)-*trans*-Carveol.



(V.) *d*(or *l*)-*cis*-Carveol.

About 47% of the product of the Ponndorf reduction of *d*-carvone consisted of the second of these alcohols. The 3 : 5-dinitrobenzoates show a marked divergence in physical properties (see table below); the *cis*-dinitrobenzoate is the more soluble, and, in general, the derivatives of the first alcohol are less soluble and have higher melting points than those of the second.

The relative reaction-velocities of the two alcohols also appear to support the above configurations. The solid alcohol reacts more slowly than its liquid stereoisomeride with *p*-nitrobenzoyl chloride: it appears permissible to ascribe this result, at least in part, to the more exposed position of the hydroxyl group in the *trans*-configuration (IV). When a mixture of the two alcohols, dissolved in pyridine, is presented with an insufficient amount of *p*-nitrobenzoyl chloride, the influences determining the distribution of this reagent are mass action and the preference of the acid chloride for one of the alcohols. This preference is expressed in an enhanced reaction-velocity. If the reaction-velocities are represented by k_t and k_c, the effect of the continually changing active masses of the three reactants is recognised in the following equation, in which *trans*- and *cis*-carveol are indicated by *t* and *c*, respectively: $k_t/k_c =$ [log (weight of *t* used) − log (weight of *t* left)]/[log (weight of *c* used) − log (weight of *c* left)]. The mean value of k_t/k_c was 1·57. *l*-Carvone, from oil of spearmint, furnished the antimeric forms of the above carveols; the two *dl*-carveols were also prepared.

The configurations of the carveols are particularly important because of their bearing upon those of the more fully hydrogenated alcohols. Since the Δ^6-double bond in carvone is reduced by sodium and alcohol in the formation of dihydrocarveols, it seemed possible that a similar reduction of each homogeneous carveol (II) would yield two dihydrocarveols (III). No reduction occurred, however; so that reduction in the case of carvone seems to depend upon the conjugation with the keto-group, which is lacking in carveol. The attempted partial hydrogenation of carveols to carvotanacetols gave indefinite results. By complete hydrogenation, each optically active carveol yielded a mixture of two optically active carvomenthols, a result which affords a configurational bridge between carveols and carvomenthols.

Although dihydrocarveols could not be prepared directly from carveols, two stereochemically homogeneous members of this family have been isolated and characterised: *d*-dihydrocarveol, $\alpha_D^{16^\circ}$ + 31·5°, by reducing *d*-carvone with sodium and alcohol; and *l*-*neo*dihydrocarveol, $\alpha_D^{14^\circ}$ − 33·2°, by reducing a purified *l*-dihydrocarvone (also obtained from *d*-carvone) with Ponndorf's reagent. The second of these was isolated by taking advantage of its relatively slow rate of reaction with 3 : 5-dinitrobenzoyl chloride. *d*-Dihydrocarveol appears to be identical with the alcohol isolated from the same mixture of four stereoisomerides by Tschugaeff (*Ber.*, 1902, **35**, 2479), by means of the laborious xanthogenamide process. The nomenclature of these two alcohols is derived from their ready and exclusive hydrogenation to *d*-carvomenthol and *l*-*neo*carvomenthol, respectively; theoretically, *d*-carvone should give rise to two other optically active dihydrocarveols, but these have not yet been isolated. *d*-*trans*-Carveol and *l*-*neo*dihydrocarveol both yield *l*-*neo*carvomenthol upon hydrogenation, and similarly *d*-*cis*-carveol and *d*-dihydrocarveol give rise to *d*-carvomenthol. Each of the carveols also yields, of course, a second carvomenthol in this process. These interesting configurational relationships will be discussed more fully in a later paper dealing with the carvomenthols. Some of the properties of the optically active unsaturated alcohols under discussion are summarised below:

	$n_D^{t^\circ}$.	$d_{4^\circ}^{t^\circ}$.	α_D (1-dcm.)	3 : 5-Dinitrobenzoate.	
				M. p.	$[\alpha]_D$, $CHCl_3$.
d-trans-Carveol	1·4942/25°	0·9484/25°	+202°	111·5°	+232°
d-cis-Carveol (m. p. 24—25°)	1·4959/25	0·9521/25	+ 22·8	92·5	− 43·8
*l-neo*Dihydrocarveol	1·4812/14	—	− 33·2	138·5	+ 6·8
d-Dihydrocarveol	1·4784/16	0·9223/16	+ 31·5	122	+ 55·2

EXPERIMENTAL.

Carveols.

d-Carvone (100 g., $[\alpha]_D$ + 62·4°), from caraway oil, was reduced in dry *iso*propyl alcohol (300 c.c.) with aluminium *iso*propoxide (40 g.), in an oil-bath at about 110°, so that 250 c.c. of a mixture of *iso*propyl alcohol and acetone distilled from the reaction vessel in 8 hours. The crude carveol (94—96 g., $\alpha_D^{16^\circ}$ + 96·0—101·2°) was extracted in the usual way and purified from unchanged carvone by treatment with hot sodium sulphite solution, as recommended by Ponndorf (*Z. angew. Chem.*, 1926, **39**, 138). Complications ensue if sodium bisulphite is used : in a typical instance, part of the product consisted of a hydrocarbon fraction (b. p. 177—178°, $n_D^{17^\circ}$ 1·4958, α_D − 12·0°),* which appeared to contain *p*-cymene and a terpene. The purified carveol (77—79 g.) had $\alpha_D^{16^\circ}$ + 100·9° to + 108·2°, b. p. 98—104°/12 mm. to 110—114°/16 mm., n_D 1·4984/16° to 1·4970/19°.

The carveol (180 g.) was then treated in pyridine solution with 3 : 5-dinitrobenzoyl chloride, and after 12 hours the mixture of carveyl 3 : 5-dinitrobenzoates was isolated and washed in chloroform solution with the usual agents. The chloroform extract was then steam-distilled; the residual ester (387 g.), which crystallised upon cooling, had $[\alpha]_D$ + 102·8° (chloroform, *c* 2·0). It was recrystallised 7 times from a mixture (1300—800 c.c.) of absolute alcohol (3 parts) and ethyl acetate (1 part). The final fraction (101 g.) of pure d-trans-*carveyl* 3 : 5-*dinitrobenzoate* consisted of short, pale brown prisms, m. p. 111·5°, $[\alpha]_D^{16^\circ}$ + 232·0° (chloroform, *c* 2·0) (Found : C, 59·3; H, 5·4. $C_{17}H_{18}O_6N_2$ requires C, 58·9; H, 5·2%). The solvent was distilled from the mother-liquors and used again. When systematically recrystallised, the material from the last four mother-liquors yielded a further quantity (26 g.) of the above ester; while that from the first three mother-liquors gave *d-cis*-carveyl 3 : 5-dinitrobenzoate (31·5 g.), m. p. 92·5°, $[\alpha]_D$ − 43·8°.

d-trans-*Carveol*.—*d-trans*-Carveyl 3 : 5-dinitrobenzoate (100 g.) was heated under reflux for 20 minutes with 5% methyl-alcoholic potassium hydroxide (460 c.c., 1·2 mols.). The mixture was steam-distilled, the receiver being changed when the drops became turbid. The 3 : 5-dinitrobenzoic acid was recovered; this cannot be done when ethyl-alcoholic alkali is used, owing to the formation of azoxy-acids (cf. Shukoff, *Ber.*, 1895, **28**, 1800). d-trans-*Carveol* had b. p. 102·2—102·4°/10 mm.; $n_D^{18^\circ}$ 1·4964, $n_D^{25^\circ}$ 1·4942; $d_{4^\circ}^{25^\circ}$ 0·9484; $[R_L]_D$ 46·70 (calc. for carveol, 46·73); $\alpha_D^{25^\circ}$ + 202·1°, $[\alpha]_D^{25^\circ}$ + 213·1°. The substance is a somewhat viscid liquid, with a disagreeable odour somewhat reminiscent of naphthalene (Found : C, 78·9; H, 10·6. $C_{10}H_{16}O$ requires C, 78·9; H, 10·6%). The *p*-nitrobenzoate had m. p. 77°, $[\alpha]_D$ + 264·4° (chloroform, *c* 2·0); the *o*-nitrobenzoate was a syrup, $[\alpha]_D$ + 110° (chloroform, *c* 2·0); the acetate had b. p. 106—106·5°/9 mm., $n_D^{14^\circ}$ 1·4770, $\alpha_D^{14^\circ}$ + 177·5°. When treated in pyridine solution with *d*-camphor-10-sulphonyl chloride, *d-trans*-carveol underwent dehydration, forming apparently a mixture of a terpene and *p*-cymene.

d-cis-*Carveol*.—Upon hydrolysing *d-cis*-carveyl 3 : 5-dinitrobenzoate with 5% methyl-alcoholic potassium hydroxide, this *alcohol* was obtained as a viscid liquid which crystallised after a few days. The broad, flat needles resembled those of *dl*-menthol. When melted and allowed to cool, the substance readily resolidified, in spite of its low melting point. The odour was pleasant, relative to that of *d-trans*-carveol, and recalled that of *d*-carvone and especially *d*-dihydrocarveol. Physical constants : m. p. 24—25°, b. p. 101·2—101·4°/10 mm.; $n_D^{18^\circ}$ 1·4980, $n_D^{25^\circ}$ 1·4959; $d_{4^\circ}^{25^\circ}$ 0·9521; $[R_L]_D$ 46·66 (calc. 46·73); $\alpha_D^{25^\circ}$ + 22·8°, $[\alpha]_D^{25^\circ}$ + 23·9° (Found : C, 78·6; H, 10·5. $C_{10}H_{16}O$ requires C, 78·9; H, 10·6%). The 3 : 5-*dinitrobenzoate* forms long, slender, yellow needles, m. p. 92·5°, $[\alpha]_D$ − 43·8° (chloroform, *c* 2·0) (Found : C, 59·2; H, 5·3. $C_{17}H_{18}O_6N_2$ requires C, 58·9; H, 5·2%). The *p*-nitrobenzoate had m. p. 26·5—28°, $[\alpha]_D$ −57·4° (chloroform, *c* 2·0). The acetate had b. p. 108—108·5°/10 mm., $n_D^{15^\circ}$ 1·4779, $\alpha_D^{15^\circ}$ + 46·4°.

Comparative Reaction Velocities of d-trans- *and* d-cis-*Carveol with* p-*Nitrobenzoyl Chloride*.—A mixture of these two alcohols (8·1 g.) having α_D +70·74° was dissolved in three times its volume of pyridine, and *p*-nitrobenzoyl chloride (5·0 g.) was added gradually with mechanical

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* All the values of α recorded in this paper are for a 1-dcm. tube.

stirring. The temperature ranged from 15° to 30° during the reaction. The recovered alcohol had α_D + 61·40°; the crude well-washed ester (6·95 g.) had $[\alpha]_D$ + 48·5° (chloroform, *c* 2·0). The value k_t/k_c, calculated from the rotatory power of the unchanged alcohol, is 1·56; calculated from the rotatory power of the crude *p*-nitrobenzoate, it is 1·58 : the mean value is thus 1·57.

l-*Carveols.*—*l*-Carvone (120 g., $[\alpha]_D^{12\cdot5^\circ}$ − 62·4°), from oil of spearmint, was reduced with aluminium *iso*propoxide over a period of 11 hours, according to the method already described. The crude carveol–carvone mixture (114 g., α_D − 111°) was converted into 3 : 5-dinitrobenzoate (208 g.) without being first treated with sodium sulphite solution. The crude ester, when fractionally crystallised from the usual mixture of absolute alcohol and ethyl acetate, yielded *l-trans*-carveyl 3 : 5-dinitrobenzoate, m. p. 111—111·5°, $[\alpha]_D$ − 230·7° (chloroform, *c* 2·0) (78 g.) and *l-cis*-carveyl 3 : 5-dinitrobenzoate, m. p. 92—92·5°, $[\alpha]_D$ + 44·2° (25 g.). In the earlier crystallisations of the *l*- or *d-cis*-ester, needles formed in the cold solution; these were collected, without unduly disturbing the mother-liquor, as soon as a material of amorphous appearance (and opposite rotatory power) began to separate. Sometimes the order of separation was reversed. Free *l-trans*- and *l-cis*-carveol possessed physical properties identical with those recorded above for the *d*-forms, except for the sense of the optical rotation. The *cis*-alcohol was readily obtained crystalline, m. p. 24—25°. The odour of *l-trans*-carveol was of the same type as that of *d-trans*-carveol, with an added suggestion of caraway; that of *l-cis*-carveol, unlike that of the enantiomeride, resembled *d*-carvone more than *d*-dihydrocarveol. The odours of the *l*-forms were feebler than those of the *d*-forms.

dl-*Carveols.*—1. Equal weights (31 g.) of *d*- and *l-trans*-carveyl 3 : 5-dinitrobenzoate were mixed in hot alcohol–ethyl acetate solution; on cooling, yellowish-brown needles of *dl-trans*-carveyl 3 : 5-dinitrobenzoate separated, m. p. 119°. Upon hydrolysis, this ester yielded *dl-trans*-carveol, b. p. 108°/16 mm., $d_4^{18^\circ}$ 0·9510, $n_D^{19^\circ}$ 1·4956, $[R_L]_D$ 46·72 (calc., 46·73). It was distinctly more viscid than the optically active forms; at − 15° it had about the consistency of ordinary glycerol at room temperature, whereas the active forms remained fairly limpid at − 15°. At − 25° *dl-trans*-carveol will scarcely flow. *dl-trans*-Carveyl *p*-nitrobenzoate crystallised from alcohol in thin and almost rectangular plates, m. p. 101°.

2. When a mixture of equal weights (11 g.) of *d*- and *l-cis*-carveyl 3 : 5-dinitrobenzoate was crystallised from hot alcohol–ethyl acetate solution, the needles of the optically active esters were replaced by elongated six-sided plates of *dl-cis*-carveyl 3 : 5-dinitrobenzoate, m. p. 91·5°. The derived *dl-cis*-carveol was a liquid, with b. p. 108°/16 mm., $n_D^{19^\circ}$ 1·4972; when immersed in a freezing-mixture, it behaved in the same way as *dl-trans*-carveol, and, unlike its components, did not crystallise. *dl-cis*-Carveyl *p*-nitrobenzoate crystallised from alcohol in thin and almost rectangular plates, m. p. 94°; it is noteworthy that the melting point of this ester is higher than that of the corresponding 3 : 5-dinitrobenzoate.

Reduction of Carveols.—1. *d-trans*-Carveol was practically unaffected when treated with sodium in dry ethyl alcohol at the boiling point.

2. *d-trans*-Carveol (8·0 g.) was hydrogenated in presence of a palladium catalyst, as used by Hughesdon, Smith, and Read (J., 1923, **123**, 2916), until 1 mol. of hydrogen had been absorbed (6 mins.). The product, which contained some terpene, yielded a 3 : 5-dinitrobenzoate (7·6 g.). After three recrystallisations this ester furnished a small quantity of an apparently impure carvotanacetyl 3 : 5-dinitrobenzoate, m. p. 109—110°, $[\alpha]_D$ + 177·5° (chloroform, *c* 2·0) (Found : C, 59·0; H, 5·8%).

3. By complete hydrogenation under suitable conditions, *d-trans*-carveol was used as a source of two new carvomenthols with $\alpha_D^{16^\circ}$ − 36·42° and + 57·56°, respectively; two other carvomenthols were derived similarly from *d-cis*-carveol : these were also prepared in other ways, and will be described in a later paper, together with some *dl*-carvomenthols.

Dihydrocarveols.

d-*Dihydrocarveol.*—*d*-Carvone, having $[\alpha]_D^{13^\circ}$ + 62·4°, from oil of caraway, when reduced with sodium and dry alcohol (Wallach, *Annalen*, 1893, **275**, 111), yielded a product which distilled mainly at 103—106°/11 mm. This fraction (82·5%) had $d_4^{16^\circ}$ 0·9250, $n_D^{16^\circ}$ 1·4826, $\alpha_D^{16^\circ}$ + 26·73°, $[\alpha]_D^{16^\circ}$ + 28·9°; it gave syrupy esters with *d*-camphor-10-sulphonic, *l*-menthoxyacetic, *p*-nitrobenzoic, and phthalic acids. The crude 3 : 5-dinitrobenzoate (204 g.) was crystalline, and had $[\alpha]_D$ + 45·2° (chloroform, *c* 2·0). Like the related 3 : 5-dinitrobenzoates, it was much more soluble in ethyl acetate than in rectified spirit, and it was fractionally crystallised from a mixture of these solvents. After 5 recrystallisations, pure d-*dihydrocarveyl* 3 : 5-*dinitrobenzoate* (94·2 g.) was obtained : m. p. 121·5—122°, $[\alpha]_D$ + 55·2° (chloroform) (Found : C, 58·9; H, 5·8. $C_{17}H_{20}O_6N_2$ requires C, 58·6; H, 5·8%). The more soluble fractions had $[\alpha]_D$ as low as + 24·9°. The ester of $[\alpha]_{\mathrm{D}}$ + 55·2°, when hydrolysed in the usual way, gave *d*-dihydrocarveol, having b. p. 106·8—107·2°/15 mm., $d_{4^\circ}^{16^\circ}$ 0·9223, $n_{\mathrm{D}}^{16^\circ}$ 1·4784, $[R_L]_{\mathrm{D}}$ 47·30 (calc., 47·24), $\alpha_{\mathrm{D}}^{16^\circ}$ + 31·5°, $[\alpha]_{\mathrm{D}}^{16^\circ}$ + 34·20. *d*-Dihydrocarveol is a viscous liquid which does not solidify even at — 25°. The odour is pleasant, sweetish, and reminiscent of *d-cis*-carveol and *d*-carvomenthol. The substance is not reduced by sodium and alcohol, but it readily yields *d*-carvomenthol when hydrogenated. The *p*-nitrobenzoate crystallises from alcohol in large, irregular plates, m. p. 37°, $[\alpha]_{\mathrm{D}}$ + 52·5° (chloroform, *c* 2·0).

l-neo-*Dihydrocarveol.*—*d*-Carvone, $[\alpha]_{\mathrm{D}}^{13^\circ}$ + 62·4° (60 g.), was reduced to dihydrocarvone with zinc dust and alcoholic potassium hydroxide (Wallach, *Annalen*, 1894, **280**, 377). The steam-distilled product (40 g.), which was not purified through the bisulphite compound, had $n_{\mathrm{D}}^{17^\circ}$ 1·4702, $\alpha_{\mathrm{D}}^{17^\circ}$ — 14·47°. After treatment with sodium ethoxide in absolute alcohol, part of the material had $n_{\mathrm{D}}^{12^\circ}$ 1·4722, $\alpha_{\mathrm{D}}^{12^\circ}$ — 13·60°. This crude dihydrocarvone (150 g.) reacted in cold aqueous-alcoholic solutions with semicarbazide acetate to yield a crystalline semicarbazone (158 g.), with m. p. 177—186°, $[\alpha]_{\mathrm{D}}$ + 26·8° (chloroform, *c* 2·0); an oily product was formed also. Two recrystallisations from methyl alcohol yielded large, transparent prisms (77 g.) with m. p. 189—190°, $[\alpha]_{\mathrm{D}}$ + 31·0°. When steam-distilled with phthalic acid (80 g.) in aqueous solution, this semicarbazone gave a ketone (43 g.) with b. p. 96—96·5°/16 mm., $n_{\mathrm{D}}^{18^\circ}$ 1·4711, $\alpha_{\mathrm{D}}^{18^\circ}$ — 16·94°. These values differ little from those of the crude ketone.

Purified *l*-dihydrocarvone (40 g., $\alpha_{\mathrm{D}}^{18^\circ}$ — 16·94°) was reduced with aluminium *iso*propoxide (20 g.) in dry *iso*propyl alcohol (200 c.c.); the reduction was complete in 6—7 hours. The distilled product (37·7 g.) had b. p. 93—97°/10 mm., $n_{\mathrm{D}}^{18^\circ}$ 1·4795, $\alpha_{\mathrm{D}}^{18^\circ}$ — 7·66°. A cooled and stirred solution in pyridine (80 c.c.) of this mixture of dihydrocarveols was treated gradually with half the calculated amount of **3** : 5-dinitrobenzoyl chloride (28·2 g.). The crude **3** : 5-dinitrobenzoate (32·5 g.) showed the following successive values of $[\alpha]_{\mathrm{D}}$ (chloroform, *c* 2·0) when recrystallised from a mixture of absolute alcohol and ethyl acetate : + 34·0°, + 42·2°, + 35·7°, + 36·4°, + 36·8° (7·6 g., m. p. 106—107°). The derived dihydrocarveol had b. p. 99—100°/13 mm., $n_{\mathrm{D}}^{15^\circ}$ 1·4800, $\alpha_{\mathrm{D}}^{15^\circ}$ + 13·50°; the odour was sweetish, and resembled that of *d*-dihydrocarveol. This alcohol was not stereochemically pure, because the derived *p*-nitrobenzoate had m. p. 75—77°, $[\alpha]_{\mathrm{D}}$ + 48·8° when crude, and m. p. 83—84°, $[\alpha]_{\mathrm{D}}$ + 33·0° after two recrystallisations.

The alcohol which remained unesterified (20·5 g.) in the above treatment with **3** : 5-dinitrobenzoyl chloride had b. p. 96—98°/12 mm., $n_{\mathrm{D}}^{18^\circ}$ 1·4796, $\alpha_{\mathrm{D}}^{18^\circ}$ — 13·26°. It was completely converted into **3** : 5-dinitrobenzoate (45 g.). After one crystallisation from a mixture of absolute alcohol and ethyl acetate, the product (31·2 g.) had m. p. 106—124°, $[\alpha]_{\mathrm{D}}$ + 19·0° (chloroform, *c* 2·0); after 5 further recrystallisations a homogeneous fraction (12·6 g.) of l-neo*dihydrocarveyl* **3** : *5-dinitrobenzoate* was obtained, with m. p. 138—138·5°, $[\alpha]_{\mathrm{D}}$ + 6·8°. This substance forms long, slender, pale yellow needles (Found : C, 58·5; H, 5·7. $C_{17}H_{20}O_6N_2$ requires C, 58·6; H, 5·8%). *l-neo*Dihydrocarveol, obtained from this ester by hydrolysis, had b. p. 101—102°/18 mm., $n_{\mathrm{D}}^{14^\circ}$ 1·4812, $\alpha_{\mathrm{D}}^{14^\circ}$ — 33·22°; the odour was distinctly unpleasant, and recalled both *d-trans*-carveol and *l-neo*carvomenthol. That the alcohol was an individual substance was shown by the behaviour of the derived *p*-nitrobenzoate : in the crude state this had m. p. 106—107°; a recrystallisation from alcohol, which reduced the weight by one-third, gave leaflets, m. p. 107°, $[\alpha]_{\mathrm{D}}$ + 14·9° (chloroform, *c* 2·0); the material recovered from the mother-liquor was practically identical with this. The *d*-camphor-10-sulphonate was obtained as a thick syrup which slowly crystallised (m. p. 91—93°); it was too soluble to permit of recrystallisation, and when heated to 125° yielded α-phellandrene and *d*-camphor-10-sulphonic acid. When hydrogenated, *l-neo*-dihydrocarveol yielded *l-neo*carvomenthol.

Derivatives of dl-*Carvenol.*

dl-Carvenone prepared from *l*-rotatory dihydrocarvone by treatment with hot aqueous sulphuric acid (Wallach, *Annalen*, 1895, **286**, 130), distilled mainly at 229—232°, and this fraction had $n_{\mathrm{D}}^{15^\circ}$ 1·4847, $[\alpha]_{\mathrm{D}}$ — 0·20°. Reduction with aluminium *iso*propoxide yielded a product with b. p. 99—102°/14 mm., $n_{\mathrm{D}}^{17^\circ}$ 1·4799. The derived **3** : 5-dinitrobenzoate had m. p. 49—59°; four recrystallisations from alcohol yielded a homogeneous dl-*carvenyl* **3** : *5-dinitrobenzoate*, which formed small yellow needles, m. p. 75—76° (Found : C, 58·4; H, 5·7. $C_{17}H_{20}O_6N_2$ requires C, 58·6; H, 5·8%). The p-*nitrobenzoate*, after purification by five recrystallisations from alcohol, formed large, thin leaflets, m. p. 65° (Found : C, 67·4; H, 6·8. $C_{17}H_{21}O_4N$ requires C, 67·3; H, 7·0%).

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