246. *The "Hydrosulphides" of Carvone and* 1-4-iso*Propyl*-Δ^2-cyclo*hexen*-1-*one.*

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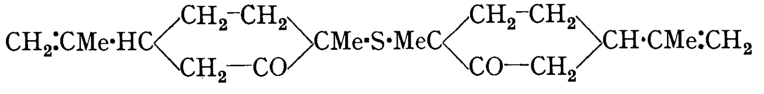
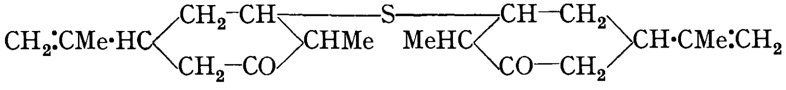
THE formation of additive compounds of αβ-unsaturated ketones and hydrogen sulphide has been observed by several workers (Fluckiger, *Ber.*, 1876, **9**, 468; Baeyer, *Ber.*, 1895, **28**, 640), the reaction in the case of carvone being particularly examined by Wallach and applied to its separation from natural sources (*Annalen*, 1899, **305**, 224). The hydrosulphide consists of two molecules of the ketone combined with one molecule of hydrogen sulphide, and it was at first suggested (Harries and Stirm, *Ber.*, 1901, **34**, 1931) that the union involved the carbonyl groups, since no oxime, semicarbazone, or phenylhydrazone could be prepared. This view was challenged by Steele (P., 1911, **27**, 240), who described the formation of a dicyanohydrin which was readily broken down to an unsaturated dinitrile. The following structures were therefore proposed:


(I.)


(II.)

These structures were later supported by the formation of a tetrabromide (Ziem, *Diss.*, Leipzig, 1912, p. 19), which has been isolated as a definite crystalline product (Challenger, Smith, and Paton, J., 1923, **123**, 1046).

The supposed hydrosulphide of *l*-4-*iso*propyl-Δ^2-*cyclo*hexen-1-one has been referred to by Wallach (*Annalen*, 1905, **343**, 32; 1907, **356**, 236) and more recently by Cahn, Penfold, and Simonsen (J., 1931, 1368), but we are of the opinion that it has not hitherto been prepared. The identity of the compound appears to have been accepted by analogy with carvone hydrosulphide, obtained by a similar method, and we have been unable to trace any analysis of the substance in the literature. It is variously described as indeterminate crystals, m. p. 121—122°, and as an amorphous solid, m. p. 82°. When prepared by the action of hydrogen sulphide on an alcoholic solution of the ketone in the presence of ammonia, a polysulphide is undoubtedly formed; but by the method outlined on p. **1149**, the pure hydrosulphide is readily obtained in a beautifully crystalline state, m. p. 206—207°. We have found the method of great service in definitely identifying the ketone in fractions of natural oils and in isolating it from such sources.

Apart from the reaction with hydrogen cyanide (Steele, *loc. cit.*), no definite proof of the presence of the keto-groups in these hydrosulphides has been forthcoming. *Bis-dinitrophenylhydrazones* of carvone and *l*-4-*iso*propyl-Δ^2-*cyclo*hexen-1-one hydrosulphides are now described, their identity being further supported by their ready breakdown to the dinitrophenylhydrazones of the parent ketones. The rotation changes in the case of these derivatives are set out below, a reversal of sign being observed on the formation of the hydrosulphide dinitrophenylhydrazones.

	d-Carvone.	*l*-4-*iso*Propyl-Δ^2-*cyclo*-hexen-1-one.
Ketone	+ 60·2°	− 64·5°
Ketone dinitrophenylhydrazone	+ 130·3	0
Hydrosulphide	+ 49·2	− 127·6
Hydrosulphide dinitrophenylhydrazone	− 172·2	+ 6·3

No direct evidence is available to fix the position of the sulphur linkings in the hydrosulphides. Wallach (" Terpene und Camphor," 1909, p. 63) preferred structure (I), but Steele (*loc. cit.*), from the easy elimination of water in the dinitrile formation, considered (II) more probable. The general behaviour of the αβ-unsaturated ketones appears to favour the latter; and the easy elimination of hydrogen sulphide finds a parallel in the ready removal of water from β-hydroxy-acids. On the other hand, the sulphur atom in the hydrosulphides is very resistant to chemical action. No sulphonium compounds are formed with alkyl halides; mercuric chloride and methyl iodide break down the dinitrophenylhydrazones of the hydrosulphides to the hydrazones of the ketones themselves; and we have also failed to achieve oxidation to a sulphoxide or sulphone. This behaviour suggests some conjugation of the sulphur atom, and the difficulty experienced in oxime, semicarbazone, and phenylhydrazone formation would meet with some explanation if the carbonyl groups were also involved. Structure (I) lends itself to such considerations if higher valencies are called into play.

EXPERIMENTAL.

d-*Carvone Hydrosulphide Bis*-2 : 4-*dinitrophenylhydrazone*.—A sample of Schering Kahlbaum carvone was carefully fractionated and had $[\alpha]_D^{18^\circ}$ + 60·2°. It was converted into the hydrosulphide by Wallach's method (*Annalen*, 1899, **305**, 224) and crystallised in silky white needles from chloroform or alcohol–chloroform, $[\alpha]_D^{20^\circ}$ + 49·2° (*c*, 5 in chloroform) [cf. Deussen and Ziem (*J. pr. Chem.*, 1914, **90**, 318), who give $[\alpha]_D^{18^\circ}$ + 48·71° (*c*, 0·6026 in chloroform)]. The m. p. of the hydrosulphide on recrystallisation was found to be 211°, but in some cases we observed a rise to 217° on further crystallisation, falling again to 211° on repetition of the process. The hydrosulphide (1 equiv.) in chloroform was added with stirring to 2 : 4-dinitrophenylhydrazine (1 g.) in alcohol (25 c.c.) containing sulphuric acid (2 c.c.), and the precipitated *bisdinitrophenylhydrazone* was recrystallised from alcohol–chloroform till of constant m. p.; orange-yellow, equidimensional crystals with more or less rectangular cross-sections, m. p. 222°, $[\alpha]_D^{20^\circ}$ − 172·2° (*c*, 1·5828 in chloroform), very soluble in chloroform, but sparingly soluble in other common organic solvents (Found : N, 16·0, 16·3; S, 4·5, 4·8. $C_{32}H_{38}O_8N_8S$ requires N, 16·1; S, 4·6%).

l-4-iso*Propyl*-Δ^2-cyclo*hexen*-1-*one* 2 : 4-*dinitrophenylhydrazone* was prepared from the ketone (obtained from *E. Cneorifolia*), $[\alpha]_D^{18^\circ}$ − 64·5°, by the same method as above; after several recrystallisations from alcohol, it was obtained as shining orange needles, m. p. 137·5—138°, and was inactive (Found : C, 56·7; H, 5·6. $C_{15}H_{18}N_4O_4$ requires C, 56·6; H, 5·7%).

l-4-iso*Propyl*-Δ^2-cyclo*hexen*-1-*one Hydrosulphide*.—Prepared according to Wallach's method, the product described as the hydrosulphide had m. p. 119° (*Annalen*, 1907, **356**, 236) or 121—122° (*Annalen*, 1905, **343**, 32) or 82° (J., 1931, 1368). Repeating the preparation, we found the product had m. p. 121°, which on standing rose to 180° (Found : S, 30%). It could not be crystallised and is evidently a polysulphide, since these also are formed in such reactions (Fluckiger, *loc. cit.*). On passing dry hydrogen sulphide into a solution of the ketone (10 g.) in absolute alcohol (100 c.c.) containing anhydrous sodium carbonate (1 g.), a crystalline product soon began to settle out, and after standing over-night, it was separated and extracted with chloroform, beautiful, colourless, equidimensional crystals with sharp pyramidal terminations being obtained on concentration. Recrystallised from alcohol–chloroform or benzene, the *hydrosulphide* had m. p. 206—207°, $[\alpha]_D^{20^\circ}$ − 127·6° (*c*, 4·425 in chloroform) (Found : S, 10·2, 10·5. $C_{18}H_{30}O_2S$ requires S, 10·3%). It is readily soluble in cold chloroform, less soluble in benzene, sparingly in cold alcohol, and moderately soluble in hot. The parent ketone is regenerated on refluxing the hydrosulphide with alkali in the presence of benzene; it was identified by its *p*-nitrophenylhydrazone, m. p. 168—169°, and 2 : 4-dinitrophenylhydrazone.

l-4-iso*Propyl*-Δ^2-cyclo*hexen*-1-*one hydrosulphide bis*-2 : 4-*dinitrophenylhydrazone* is readily prepared as described in the preceding cases. Recrystallised from chloroform or alcohol–chloroform, it separates as yellow needles, m. p. 238—239°, $[\alpha]_D^{20^\circ}$ + 6·35° (*c*, 1·419 in chloroform) (Found : N, 16·8; S, 4·9, 4·8. $C_{30}H_{38}N_8O_8S$ requires N, 16·7; S, 4·8%).

Reactions with mercuric chloride. (*a*) Challenger, Smith, and Paton (*loc. cit.*) observed that in chloroform solution carvone hydrosulphide reacted with ethereal mercuric chloride to precipitate a yellow solid (probably $2HgS,HgCl_2$), a residual oil (probably carvone) being isolated from the filtrate. We have repeated this observation and identified the oil as carvone by conversion into its 2 : 4-dinitrophenylhydrazone, m. p. (and mixed m. p.) 191—191·5°, $[\alpha]_D^{20^\circ}$ + 130·4° (*c*, 2·025 in chloroform) (Allen, *J. Amer. Chem. Soc.*, 1930, **52**, 2955, gives m. p. 189°).

(*b*) *l*-4-*iso*Propyl-Δ^2-*cyclo*hexen-1-one hydrosulphide gave a similar breakdown on the same treatment, the ketone being isolated and identified by its *p*-nitrophenylhydrazone.

(*c*) *d*-Carvone hydrosulphide bisdinitrophenylhydrazone also reacts with ethereal mercuric chloride, but the reaction is only completed after several days' standing. The residue on evaporation of the filtrate was recrystallised from alcohol and identified as carvone 2 : 4-dinitrophenylhydrazone

(*d*) The bis-2 : 4-dinitrophenylhydrazone of *l*-4-*iso*propyl-Δ^2-*cyclo*hexen-1-one hydrosulphide behaved similarly, but the reaction was hastened by 2—3 hours' refluxing. The dinitrophenylhydrazone of the ketone was recovered from the filtrate.

Action of methyl iodide. Previous attempts to prepare a sulphonium derivative by the action of methyl iodide on carvone hydrosulphide were unsuccessful. On refluxing its bisdinitrophenylhydrazone with excess methyl iodide for 11 hours, we found that the reaction mixture contained some unchanged material together with *d*-carvone 2 : 4-dinitrophenylhydrazone.

Attempted oxidation. Carvone hydrosulphide was recovered unchanged after prolonged treatment of an acetone solution with hydrogen peroxide. Some decomposition to carvone appears to take place, as the mother-liquors smelt faintly of the ketone, but it was not isolated.

In other experiments the bisdinitrophenylhydrazone of *l*-4-*iso*propyl-Δ^2-*cyclo*hexen-1-one hydrosulphide was shaken in chloroform solution with aqueous permanganate during 2 days, and thereafter for 6 hours in a mechanical shaker, but only unchanged material was isolated.

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