301. *The Reaction of Sulphur and Sulphur Compounds with Olefinic Substances. Part III. The Reaction of Sulphur with Squalene.*

By George F. Bloomfield.

Sulphur reacts with squalene in a manner very similar to that observed with dihydromyrcene, and an intramolecularly-linked unimolecular sulphide as well as an intermolecularly-linked polysulphide is obtained.

Rather prolonged reaction times are necessary to obtain an appreciable degree of sulphuration of squalene, $H\cdot[CH_2\cdot CMe{:}CH\cdot CH_2]_3[CH_2\cdot CH{:}CMe\cdot CH_2]_3\cdot H$, below 140° in the absence of auxiliary activating substances, and, as might be expected, the course of the reaction shows a marked resemblance to the sulphuration of dihydromyrcene. The crude reaction product consists of unreacted squalene of undiminished olefinic unsaturation, together with a unimolecular sulphurated product and a bimolecular polysulphide. Of the two sulphurated components, the unimolecular product, which cannot be completely freed from unreacted squalene, is present in the major proportion, although the sulphur which enters into reaction is distributed fairly equally among the two components. The unimolecular product, $C_{30}H_{50}S$, in which one sulphur atom has become incorporated in the squalene molecule with the loss of one double bond, is substantially free from sulphydryl sulphur, and contains carbon and hydrogen in the same ratio as in the original hydrocarbon. The bimolecular product is a polysulphide of squalene, $C_{60}H_{100}S_6$, of considerable stability towards sodium sulphite, and the ratio of hydrogen to carbon is again that of the parent hydrocarbon; the incorporation of sulphur is accompanied by loss of olefinic unsaturation. The unsaturation of the bimolecular product undergoes a further reduction on heating at temperatures exceeding 140°.

In view of the known sensitivity of the reaction of sulphur with olefins towards quite small proportions of certain activating substances, it is of considerable interest that the addition of mercaptobenzthiazole and a zinc soap to the sulphur–squalene system results only in increased yields in both uni- and bi-molecular products without greatly affecting their relative proportions, provided that the time and temperature conditions of the reaction remain unaltered.

Experimental.

Microanalyses were carried out by Dr. W. T. Chambers and Miss H. Rhodes. Olefinic unsaturation was determined by bromine addition (Bloomfield, *J. Soc. Chem. Ind.*, 1945, **64**, 274), and molecular weights were determined by depression of f. p. of benzene.

Squalene (14 g.) was heated with sulphur (1·4 g.) in an atmosphere of nitrogen for 3 hrs. at 140°. The product was freed from unreacted sulphur first by cooling and filtering, and finally by passage through a falling-film molecular still (Farmer and Sutton, *ibid.*, 1946, **65**, 164) at 100°. Subsequent molecular distillation of the product at 140° gave a pale yellow distillate (13 g.) having $n_D^{17^\circ}$ 1·5031 (Found: C, 86·1; H, 12·0; S, 2·1; ·SH, 0·09; I.V., 338; *M*, 412. Calc. for mixture of 71% $C_{30}H_{50}$ and 29% $C_{30}H_{50}S$: C, 85·7; H, 12·2; S, 2·1; I.V. 348; *M*, 420) which showed selective U.V. absorption at 2800 A., and a reddish-brown viscous residue (1·5 g.) (Found: C, 71·15; H, 9·95; S, 18·75; ·SH, 0·3; I.V., 250 ± 15; *M*, 825. $C_{60}H_{100}S_6$ requires C, 71·1; H, 9·95; S, 18·95%; *M*, 1013). A 10% aqueous solution of sodium sulphite removed 9% of the sulphur contained in the residue in 3 hrs. at 100°, but was without action on the sulphur in the distillate. A sample of the residue was heated in a vacuum for 45 mins. at 160° (Found: C, 70·9; H, 9·9; S, 18·7; ·SH, 0·9%; I.V., 209). Further molecular distillation of the distillate at 110° yielded fractions respectively poorer (Found: S, 1·2%)

and richer (Found : S, 4·8%; *M*, 415) in the sulphurated component. The former of these two fractions yielded substantially pure squalene, $n_D^{20°}$ 1·4988 (Found : S, 0·4%; I.V., 360) on passage through chromatographic alumina on which the sulphurated component was strongly adsorbed.

Squalene (10 g.), sulphur (1·0 g.), zinc oxide (0·5 g.), stearic acid (0·5 g.), and mercaptobenzthiazole (0·1 g.) were heated together for 3 hrs. at 140°. Separative treatment in the molecular still yielded a distillable component (8·4 g.), $n_D^{19°}$ 1·5109 (Found : C, 83·15; H, 11·6; S, 5·3; active H, <0·01; I.V., 312; *M*, 413. Calc. for 73% $C_{30}H_{50}S$ + 27% $C_{30}H_{50}$: C, 83·1; H, 11·7; S, 5·3%; I.V., 311; *M*, 434) and a residue (1·0 g.) (Found : S, 19·95%) which was free from zinc.

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The British Rubber Producers' Research Association,
Welwyn Garden City, Herts.

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