Table 1.

	Per cent epicuticle (approx.)	% O	% S	% N	% Br
Residue from Na_2S-treatment	10	22.3	3.5	14.3	
Sample obtained by brominating the wool	30	27.0	3.0	13.0	8.3
Untreated wool	0.1–0.2		2.8	14.7	

constituents such as proteins or possibly fatty acids. — The X-ray diagrams from samples isolated from wool give some interferences found neither in the α- nor in the β-diagram of wool [10], which are possible indications of structures of the above mentioned type.

As to the modification caused by the chemical treatment Table 1 should give an idea and at the same time give a few figures for the chemical composition of the epicuticle compared with ordinary wool. The elementary analysis has been carried out by the Microchemical Laboratory of the Medico-Chemical Institute of The University of Uppsala.

The nitrogen content of the epicuticle seems to be lower than that of the main part of the wool, the sulphur content is slightly higher. In the case of the Na_2S-treated sample some impurities may originate from polysulphides and sulphur containing products formed by the reagent and the original material. In the brominated sample it is evident that the bromine has reacted with the organic material. Moreover it is indicated that some oxidation has occurred as the oxygen content is higher than in the other samples. This oxidation may have led to the formation of carboxyl groups which may be an explanation to the fact that samples obtained in this way are to great extent soluble in dilute alkali.

This investigation, sponsored by a research fellowship from the International Wool Secretariat to one of us (G. L.), is beeing continued.

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Investigations in the Retene Field. IV. Nitration of Retene in the Presence of Boron Trifluoride

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Several attempts have been made to prepare nitro-derivatives of retene by direct nitration, the most successful being those reported by Fredriksen and Nielsen [1] (who also give further references on this subject). By nitration of retene under mild conditions these workers obtained a crude product from which they isolated 9-nitroretene in a yield of about 5 %. According to a private communication, they were also able to isolate 3-nitroretene but this

compound was obtained in a very low yield. These mononitroretenes were separated from the reaction product by chromatography and molecular destillation. During the chromatography they observed several zones including a purple one and a yellow one, and it was from the latter that the two nitroretenes were isolated.

As it was of interest to establish what is actually formed when nitric acid reacts with retene we have repeated the nitration and examined the products rather more closely. Analyses showed that the purple zone on the chromatograms probably does not contain significant amounts of nitroretenes, whereas the yellow one consists chiefly of mononitroretenes, in amount corresponding to a yield of about 50 % of the theoretical.

In an attempt to obtain higher yields of mononitroretenes we have carried out some nitrations in the presence of boron trifluoride, a substance which is known to be a remarkable catalyst for many organic reactions including the nitration of aromatic hydrocarbons [2]. Using this catalyst it is often possible to nitrate organic compounds quickly and almost completely with stoichiometric amounts of nitric acid. In the presence of boron trifluoride, the nitration of retene was nearly complete after a few minutes at 80—90° C when only 1.05 moles of nitric acid/mole of retene were used. Chromatography of the reaction product revealed several zones, showing that many compounds are formed in the reaction. However, the mixed mononitroretenes accounted for the major portion, and were obtained in yields corresponding to 80—83 % of the theoretical. Some experiments were carried out in the absence of boron trifluoride and showed that, at this temperature, the mixture of mononitroretenes could be obtained in a yield of about 65 %, if 1.5 moles of nitric acid/mole of retene were used and the reaction time was prolonged to 15—25 minutes. With smaller amounts of nitric acid, much retene could be recovered unchanged.

This preliminary investigation of the nitration of retene indicates that mononitroretenes can be obtained in good yields by direct nitration of the hydrocarbon. The problem still to be solved is the separation of the different mononitroretenes. It may be mentioned that the mixture of mononitroretenes can be isolated in reasonably good yield by destillation of the crude reaction product under reduced pressure.

Experimental. Retene (5.0 g, m.p. 95°C) was dissolved in glacial acetic acid (50 ml) containing boron trifluoride (1.4 g), at 80—90 °C, and a solution of conc. (99—100 %) nitric acid (1.4 g) and boron trifluoride (1.4 g) in glacial acetic acid (10 ml) was added with stirring during 2—5 minutes. The mixture was poured into cold (0—5 °C) water immediately, and the precipitate which formed was filtered off, washed with cold water, and dissolved in benzene. The benzene solution was washed with dilute alkali and water and evaporated, and the residue, a viscous red-brown oil, was dissolved in a mixture of 10 vol. of petroleum ether (b. p. 40—60 °C) and 1 vol. of benzene and adsorbed on a column (2 × 25 cm) of alumina. The same solvent mixture was used to elute the yellow zone containing mononitroretenes. Evaporation of the solvents gave a yellow viscous oil (5.4 g) which contained some unchanged retene and other impurities, and was chromatographed again on a column (3.5 × 25 cm) of alumina. Retene was eluted with pure petroleum ether, then the mononitroretenes were eluted with the same solvent mixture as above. Evaporation of the solvents yielded the mononitroretenes as a yellow viscous oil, (4.9 g, 83 % of the theoretical yield).

$C_{18}H_{17}NO_2$ (279.3)

Calc.	C 77.4	H 6.14	N 5.0
Found	» 77.9	» 6.19	» 5.2

Titration with $TiCl_3$:

Found Molecular weight 281

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