The Unsymmetrical Coupling of Geraniol

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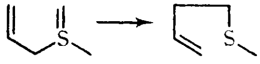
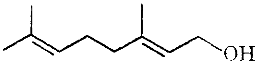
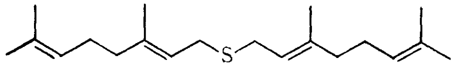
RECENTLY we,[1] and others,[2] have reported the rearrangement of vinyl sulphonium ylids, in the manner of the general scheme (I), and have commented on the possible significance of this process in enzymic reactions. To demonstrate its use in the formation of carbon–carbon bonds between allyl systems, we applied the reaction to a molecule of much larger molecular weight, namely geraniol (II).

Geraniol (II), transformed to the chloride† with thionyl chloride in pyridine,[3] and subsequently coupled with sodium sulphide, gave the symmetrical sulphide (III), b.p. 170—176° (0·06 mm. Hg) n.m.r. δ 5·20 (m, 4H, vinyl), 3·04 (d, J 7·5, 4H, CH_2–S), 2·06 (m, 8H, CH_2), and 1·65 (m, 18H, vinyl CH_3), further purified by chromatography over silica gel. Alkylation with triethyloxonium fluoroborate[1] proceeded to the corresponding ethyl sulphonium salt, which was smoothly rearranged with potassium t-butoxide in benzene to the sulphide (IV), ν_{max} 909 cm.$^{-1}$, n.m.r. δ 5·9—5·12 (m, 6H, vinyl) 3·22 (m, 1 H, S–CH), 2·32 (q, 2 H, S–CH_2), 2·07 (m, 6 H, vinyl CH_2), 1·65 (m, 18 H, vinyl CH_3), 1·0—1·4 (m, 12 H), mass spectral molecular weight 334. Desulphurization of (IV) was readily achieved by means of sodium in ammonia and the resultant hydrocarbon (V),‡ n_D^{22} 1·4842, ν_{max} 910 cm.$^{-1}$, n.m.r. δ 5·73—4·9 (m, 6 H, vinyl), 1·97 (m, 8 H, vinyl CH_2), 1·60 (m, 15 H, vinyl CH_3), 1·3 (m, 2 H, CH_2) and 0·93


(I)


(II)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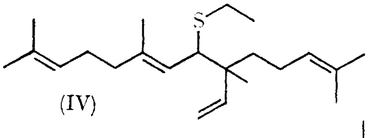
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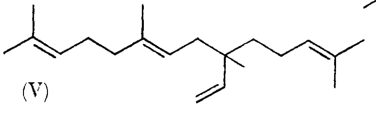
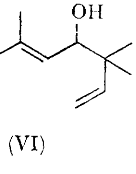

(V)


(VI)

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† Shown by n.m.r. to contain 30% of linalyl chloride.

‡ Satisfactory analytical data have been obtained for all new compounds.

(s, 3H, CH_2), mass spectral molecular weight 274, was separated from a little unchanged sulphide (IV) by chromatography over silica gel. This example demonstrates the ease with which relatively large, unsymmetrically coupled, hydrocarbons can be made by this method. It is of interest to note that this same carbon skeleton, at the monoterpene level, is found in the unusual terpenoids of the Artemisia oil, *e.g.* artemisia alcohol (VI).[4]

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[3] M. O. Forster and D. Cardwell, *J. Chem. Soc.*, **1913**, **1338**.

[4] T. Takemoto and T. Nakajuna, *J. Pharm. Soc. Japan*, **1957**, **77**, **1310** (*Chem. Abs.*, **1958**, **52**, **4478**).