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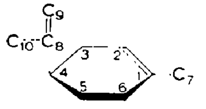
THE REACTION OF SULPHUR AND SULPHUR COMPOUNDS WITH OLEFINIC SUBSTANCES—XIII*

THE MECHANISM OF INTERACTION OF SULPHUR WITH (+)-LIMONENE

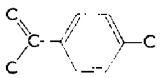
C. G. Moore and M. Porter
The British Rubber Producers' Research Association,
Welwyn Garden City, Herts, England

Abstract—The reaction of sulphur with (+)-limonene (I) to give the hydrocarbons (II) and (III), and the cyclic sulphides (+)-(IV), (−)-(V), and optically inactive (VI), as demonstrated by Weitkamp,[1-3] is shown to be uniquely consistent with a recently advanced polar mechanism of olefinic sulphuration.[5,6]

Weitkamp[1-3] has shown that reaction of sulphur with (+)-limonene (I) at 140–170°C yields *p-iso*propenyltoluene (II), *p*-cymene (III); the cyclic sulphides (+)-(IV), (−)-(V), and optically inactive (VI); and an unresolved "limonene" polysulphide. The stereochemical relationships between the reactant (I) and the cyclic sulphides (IV)–(VI) were convincingly established, but no detailed or acceptable mechanistic explanation was offered for the formation of the various products.



I



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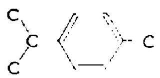

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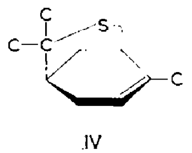

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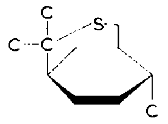

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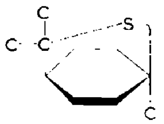
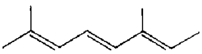


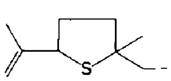
VI

The sulphuration of (I) to give (II)–(VI) is analogous to the sulphuration of 2:6-dimethylocta-2:6-diene (VII) to give (VIII)–(XII),[4] products which are explicable

VII



VIII



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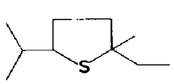
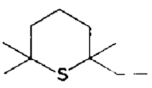


X



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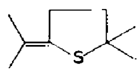

XII

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* Part XII, L. Bateman, R. W. Glazebrook and C. G. Moore, *J. Polymer Sci.* In press.

[1] A. W. Weitkamp, *Preprints of papers presented before the Division of Petroleum Chemistry, San Francisco Meeting*, 13–18 April, p. 253. American Chemical Society (1958).

[2] A. W. Weitkamp, *Preprints of papers presented before the Division of Petroleum Chemistry, San Francisco Meeting*, 13–18 April, p. 259. American Chemical Society (1958).

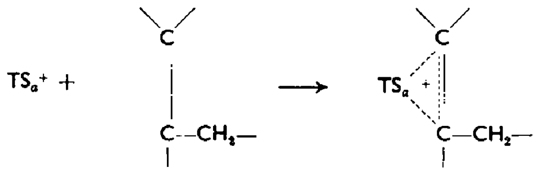
[3] A. W. Weitkamp, *Preprints of papers presented before the Division of Petroleum Chemistry, San Francisco Meeting*, 13–18 April, p. 263. American Chemical Society (1958).

L. Bateman, R. W. Glazebrook and C. G. Moore, *J. Chem. Soc.* 2846 (1958).

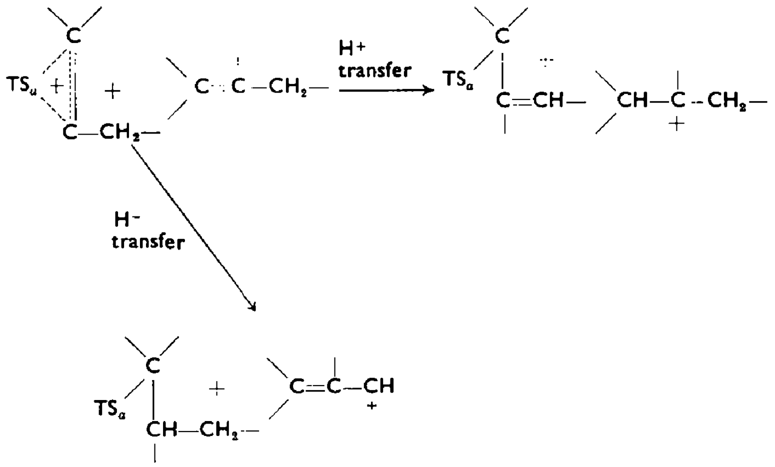
on the basis of a recently proposed *polar* mechanism,[5,6] the general features of which are given by reactions (1)–(7):

$$TS_a{-}S_bT \longrightarrow TS_a^+ \;.\,.\,.\,.\,.\,.\,.\; {}^-S_bT \qquad (1)$$

(Polysulphide, where
T = alkyl or alkenyl
group and $a,b > 1$)

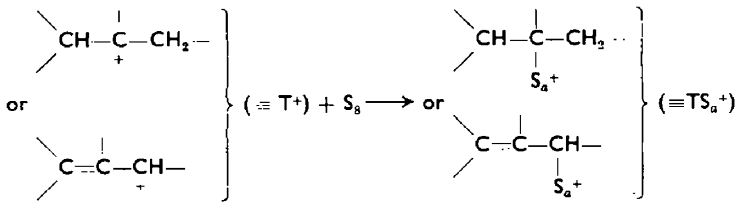


(2)



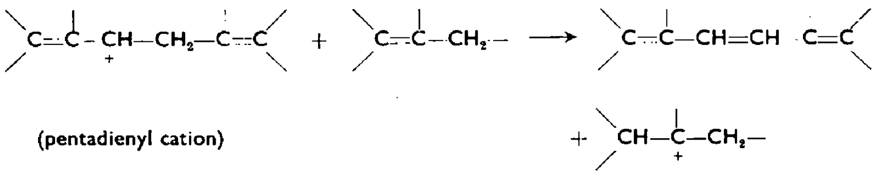
(3)

(4)



(5)

(6)



(7)

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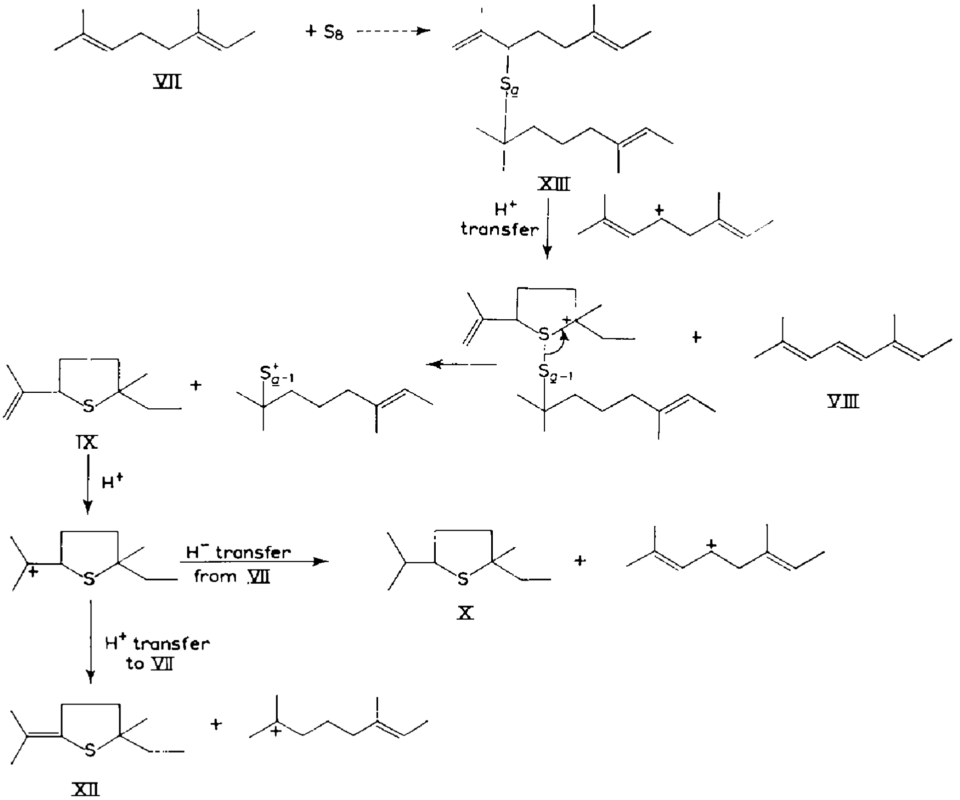
[5] G. W. Ross, *J. Chem. Soc.* 2856 (1958).

[6] L. Bateman, C. G. Moore and M. Porter, *J. Chem. Soc.* 2866 (1958).

The compounds (VIII)–(XII) result from subsequent reactions of initially formed polysulphides, as exemplified by the formation of (VIII), (IX), (X), and (XII) from the polysulphide (XIII) (Reaction scheme A).

Reaction scheme A



The above polar mechanism is now applied to explain the formation of (II)–(VI) from (+)-limonene (I), as expressed in Reaction scheme B in which reactions leading to the initial polysulphides (XIV)–(XVI) are restricted to the more reactive, trialkylethylenic, double bond of the (+)-limonene (cf. ref. 5). The two stereoisomeric polysulphides (XIV) and (XV) will predominate over the structural isomer (XVI), in keeping with the preferential formation of an *endo*- rather than *exo*-cyclic olefinic double bond in a six-membered ring system.[7] The cyclic sulphides (IV) and (VI) then result from protonation of the *iso*propenyl groups of (XV) followed by intramolecular heterolysis of an S—S bond by the *iso*propylium ion centre, as depicted in the scheme. The polysulphide (XIV) can act similarly as the precursor to (IV), but it cannot yield (VI) because of the *trans*- configuration of the *iso*propenyl and —S_a— substituents in the *cyclo*hexane ring. The cyclic sulphide (IV) is converted to (V) by an initial protonation reaction to give the carbonium ion (XVII) which then undergoes a stereospecific hydride ion (H^-) transfer from a suitable hydrogen donor, e.g. (I), to give (V). The stereospecificity of this H^- transfer will be assisted firstly, by interaction of the

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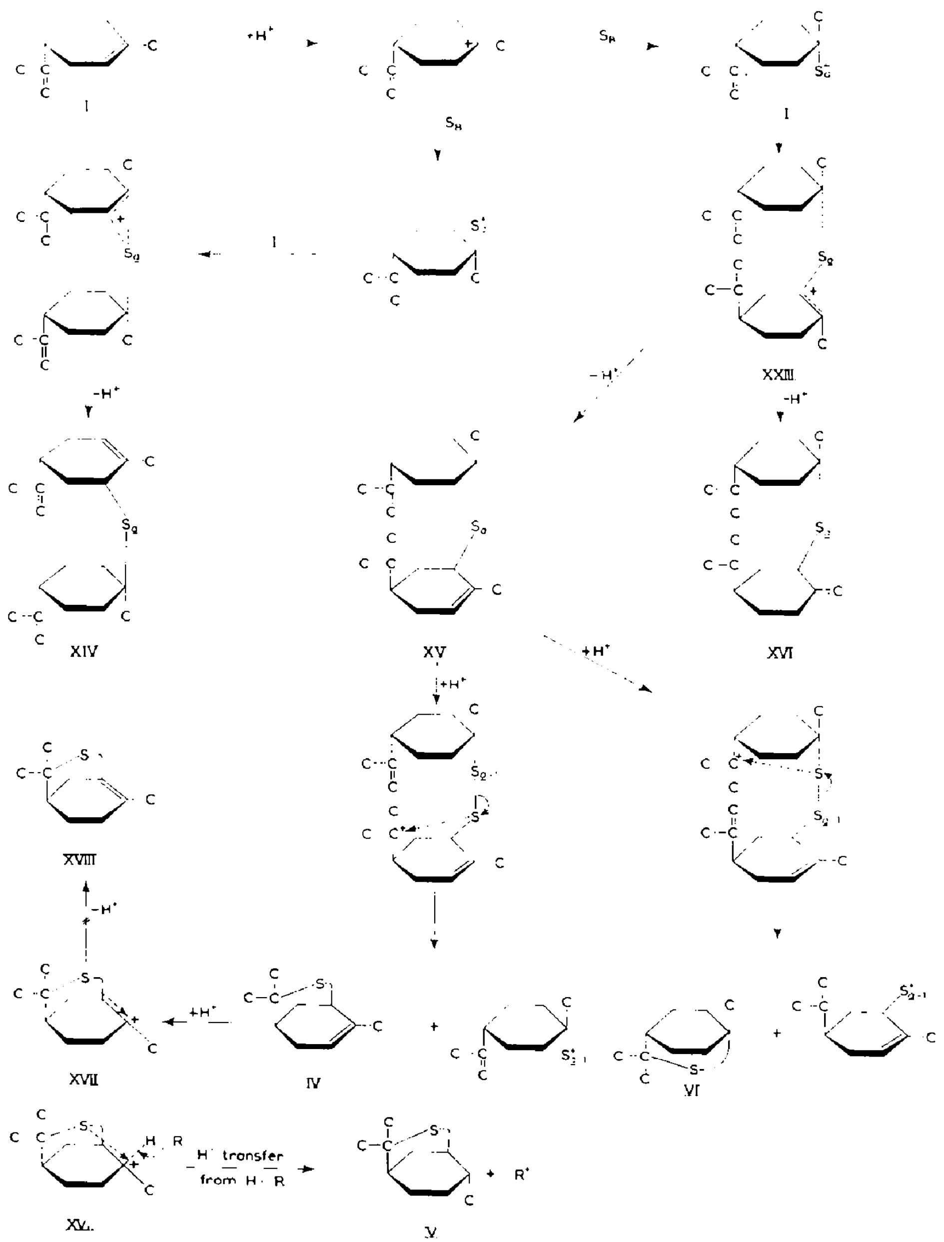
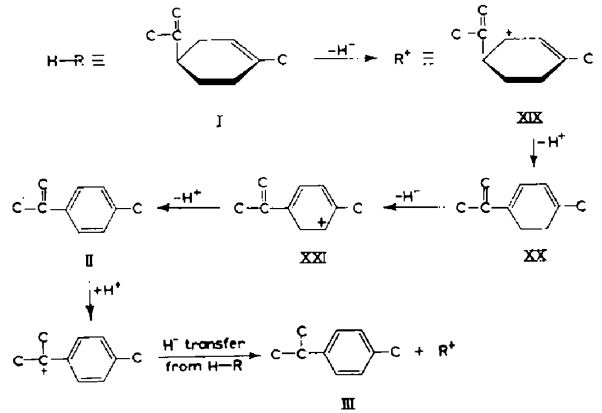
[7] R. B. Turner and R. H. Garner, *J. Amer. Chem. Soc.* **80**, 1424 (1958).

carbonium ion centre in (XVII) with the sulphur atom of the thia*cyclo*pentane ring, leading to a preferred partial *trans*- configuration of the C_1—CH_3 and C_2—S— groups in the *cyclo*hexane ring of (XVII); and secondly, by the occurrence of greater steric hindrance when the above C_1—CH_3 and C_2—S— groups are in a *cis*- configuration, as revealed by molecular models. The formation of (V) from (IV), as required by the mechanism now proposed, is consistent with Weitkamp's finding[2] that the yield of

Reaction scheme B



Reaction scheme B (continued)



(IV) decreases at the expense of (V) as the sulphuration reaction proceeds. The non-formation of the vinyliccyclic sulphide (XVIII), analogous to (XII) obtained from the acyclic 1:5-diene (VII), is explicable on the basis of the known instability of fused-bicyclic systems containing a bridgehead double bond (Bredt's Rule).[8] The fact that sulphuration of (+)-limonene yields optically active cyclic sulphides (+)-(IV) and (—)-(V) is also consistent with the proposed mechanism since the asymmetric centre at C_4 in the (+)-limonene is not destroyed in the reactions leading to (IV) and (V). It is also noteworthy that because of the stereochemical restrictions which must be imposed on the reaction intermediates which finally yield (IV) and (V) then additional centres of optical activity will be introduced into the latter two compounds, viz. at C_2 in (IV) and at C_1 and C_2 in (V). The hydrocarbons (II) and (III) are formed by a sequence of hydride ion- and proton-transfer processes analogous to those leading to the conjugated triene (VIII) from the 1:5-diene[6] (VII) (Reaction schemes A and B). The deprotonation of the mesomeric alkenyl cations (XIX) and (XXI) according to reaction (7) in preference to their alternative reaction with sulphur, reaction (6), is explicable on the basis of the energy gained from the formation of the conjugated hydrocarbons (XX) and (II), respectively.

The occurrence of initial sulphuration processes at the less reactive *iso*propenyl group of (+)-limonene, comparable to those detailed in Reaction scheme B, will lead to additional polysulphides, e.g. (XXII) in which the dotted lines represent alternative positions of the double bond. Further, if the intermediate cyclic persulphonium ions such as (XXIII) are stabilised by hydride ion transfer, reaction (4), as an alternative to deprotonation, reaction (3), then polysulphides such as (XXIV) will be formed. It is significant, however, that the polysulphides (XXII) and (XXIV) will not yield, by subsequent reactions analogous to those of Reaction scheme B, any alternative cyclic sulphides to those observed experimentally. Thus, both polysulphides will give (VI), but the substituted thia*cyclo*heptanes (XXV) theoretically derivable from (XXII) are unlikely to be formed because of unfavourable steric factors associated with the seven-membered ring and the bridgehead double bond.

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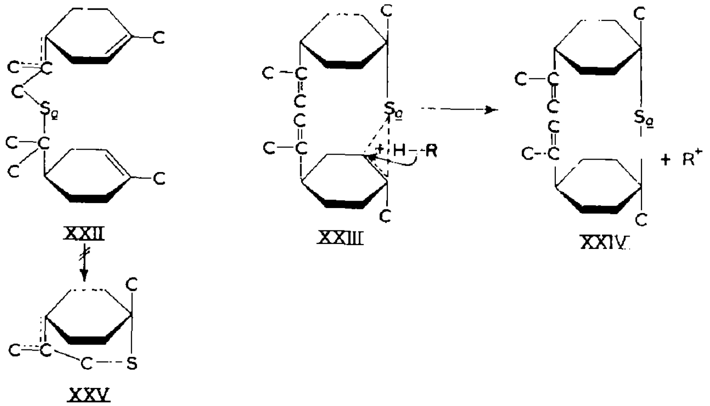
[8] F. S. Fawcett, *Chem. Rev.* 47, 219 (1950).



In conclusion, the experimental data of Weitkamp[1–3] provide critical support for the polar mechanism of olefinic sulphuration[5,6] which specifically explains the formation of the observed products (II)–(VI) from (+)-limonene, and of equal importance, does not predict any additional cyclic sulphide structures.

This work forms part of the programme of research undertaken by the Board of The British Rubber Producers' Research Association.