

ACID- AND BASE-CATALYSED TRANSFORMATIONS OF *m*-MENTHADIENES

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VERY little information¹⁻³ is available on the behaviour of *m*-menthadienes towards acid- and base-catalysts. For that reason we subjected *d*-*m*-mentha-1(6), 8-diene [*d*-sylvestrene] (I), *m*-mentha-1(6), 3(8)-diene [isosylvestrene] (II) and *m*-mentha-1, 3(8)-diene [sylveterpinolene] (III) to the action of trichloroacetic acid and potassium *t*-butoxide, catalysts already tested in the *p*-menthadiene field⁴⁻⁶.

Adopting essentially the procedure recommended for (+)-limonene⁴, the *m*-menthadienes were processed with trichloroacetic acid [Table I (A)].

isopropylidene derivatives, (III), is formed ~ 7 times that of (II).

Upon reacting isosylvestrene with trichloroacetic acid, the dominant reaction is conjugation to (III) (71%); the isopropenyl derivatives (I), (IV) and (V) amount to a total of only 13.5%. Clearly then, one of the routes of generating (III) from (I) is through (II).

On the other hand, the reactivity profile of sylveterpinolene is in marked contrast to the above two *m*-menthadienes. Being a conjugated diene, it displays considerable stability; only 56% of the

TABLE I
Transformations of m-menthadienes

Terpene* (Kind)	Catalysate			Analyses by g.l.c. (%)						
	Yield	n_D^{20}	$(\alpha)_D^{30}$	I ^a	II ^b	III ^c	IV	V	VI	VII ^d
(I)	2.3	1.5059	$\pm 0^\circ$	3.0	5.1	36.2	15.0	2.0	6.1	23.9
(II)	2.9	1.5047	$\pm 0^\circ$	3.4	5.0	71.0	4.8	5.3	0.5	10.0
(III)	1.9	1.5061	$\pm 0^\circ$	2.0	2.4	44.2	6.0	..	0.2	30.2
B										
	Catalyst: Potassium <i>t</i> -butoxide† in DMSO‡; 85 ± 2°; 3 hr									
(I)	3.7	1.4962	$\pm 24.7^\circ$	45.6	5.5	45.0	3.0	0.9
(II)	4.0	1.5051	$\pm 0^\circ$	12.2	8.2	73.0	4.3	2.3
(III)	3.9	1.5107	$\pm 0^\circ$	2.4	6.1	82.0	6.5	2.4
				R_f 0.73	0.88	0.86	0.76	0.30	0.93	0.90

* 0.0031 mole; ** 0.031 mole; † 0.06 mole; ‡ 50 ml.

Tetrabromide, m.p. and mixed m.p.: (a) 137–138°; (b) 127–128°; (c) Maleic anhydride adduct m.p. and mixed m.p.: 306–308°; (d) n.m.r. (CCl₄): δ (7.0) (aromatic protons), further characterised by oxidation to isophthalic acid (dimethylester¹⁵, m.p. and mixed m.p. 64–65°).

Qualitatively the catalysates obtained are composed of (I), (II), (III), *m*-mentha-1, 8-diene [isylvestrene] (IV), *m*-mentha-1(7), 8-diene (V), *m*-menth-1-ene (VI) and *m*-cymene (VII). Nevertheless, the data throw light on the comparative stability and reactivity of these *m*-menthadienes.

Contrary to the belief that sylvestrene is stable⁷, only 3% of the hydrocarbon survived reorganisation. The proportion of isopropylidene to isopropenyl derivatives is in the approximate ratio 2:1 which reflects that in (I) the *exo* is more labile than the *endo* double bond. The shift of the nuclear double bond favours the liberation of (IV) (15%) rather than of (V) (2%)⁸. Of the

hydrocarbon suffered transformation. The endocyclic double bond wandered reluctantly within the ring to furnish (I) (2%) and (IV) (6%) but refused to migrate to the exocyclic position to afford (V).

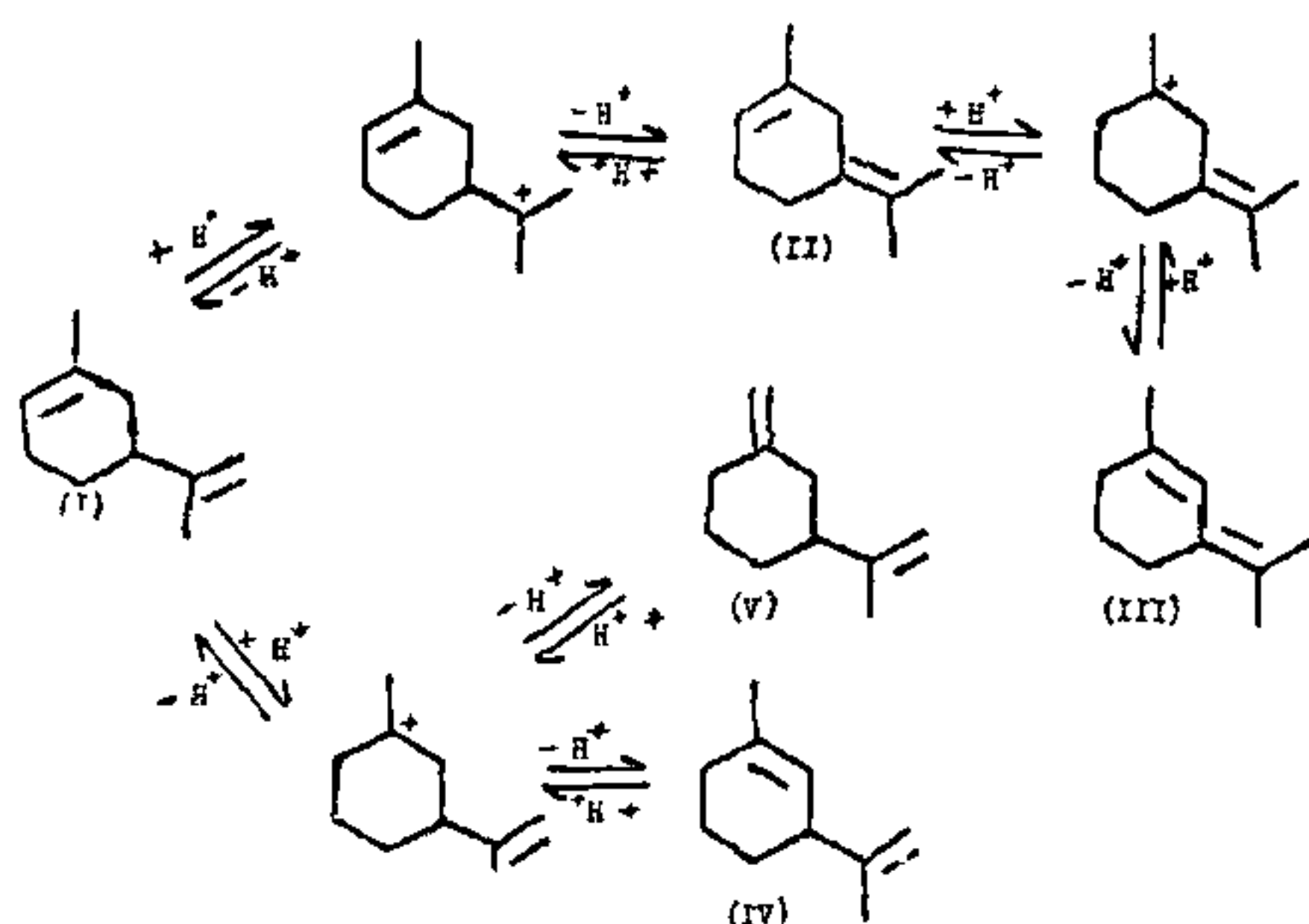
The isomerisations are accompanied by disproportionation to *m*-cymene (VII) and *m*-menth-1-ene (VI). Sylveterpinolene underwent maximum conversion to *m*-cymene (~ 30.2%). Since, in the catalysates, (III) is the richest species, it stands to reason that hydrogen transfer might have occurred mainly through this hydrocarbon, even though the participation of other *m*-menthadienes is not excluded.

For the base-catalysed reactions, the *m*-menthadienes were vigorously stirred and heated in an atmosphere of nitrogen with potassium *t*-butoxide in DMSO [Table I(B)].

Under the experimental conditions, the reactivity of these *m*-menthadienes is of the order (II) > (I) > (III). Only 18% of (III) has been changed to other isomers, again substantiating its great stability. Sylveterpinolene is the major product of isomerisation of (I) and (II), the yield being respectively 45% and 73%. This is in accord with the fact that base-catalysed isomerisations stimulate conjugation⁹. As in acid-catalysed isomerisations, the data suggest the reaction sequence: (I) → (II) → (III). Only superficial conversion of these *m*-menthadienes to sister isomers (IV) and (V) has taken place. The most distinguishing feature of the base-catalysed reactions is that the isomerisates are remarkably free from products of disproportionation¹⁰.

In general, the present investigation has clearly established the interconvertibility of (I), (II) and (III).

The acid-catalysed transformations can be adequately explained by assuming the intermediate formation of carbonium ions¹¹. Thus, the steps leading to the four isomers (II)–(V) from *d*-sylvestrene (I) can be pictured as in Scheme I.



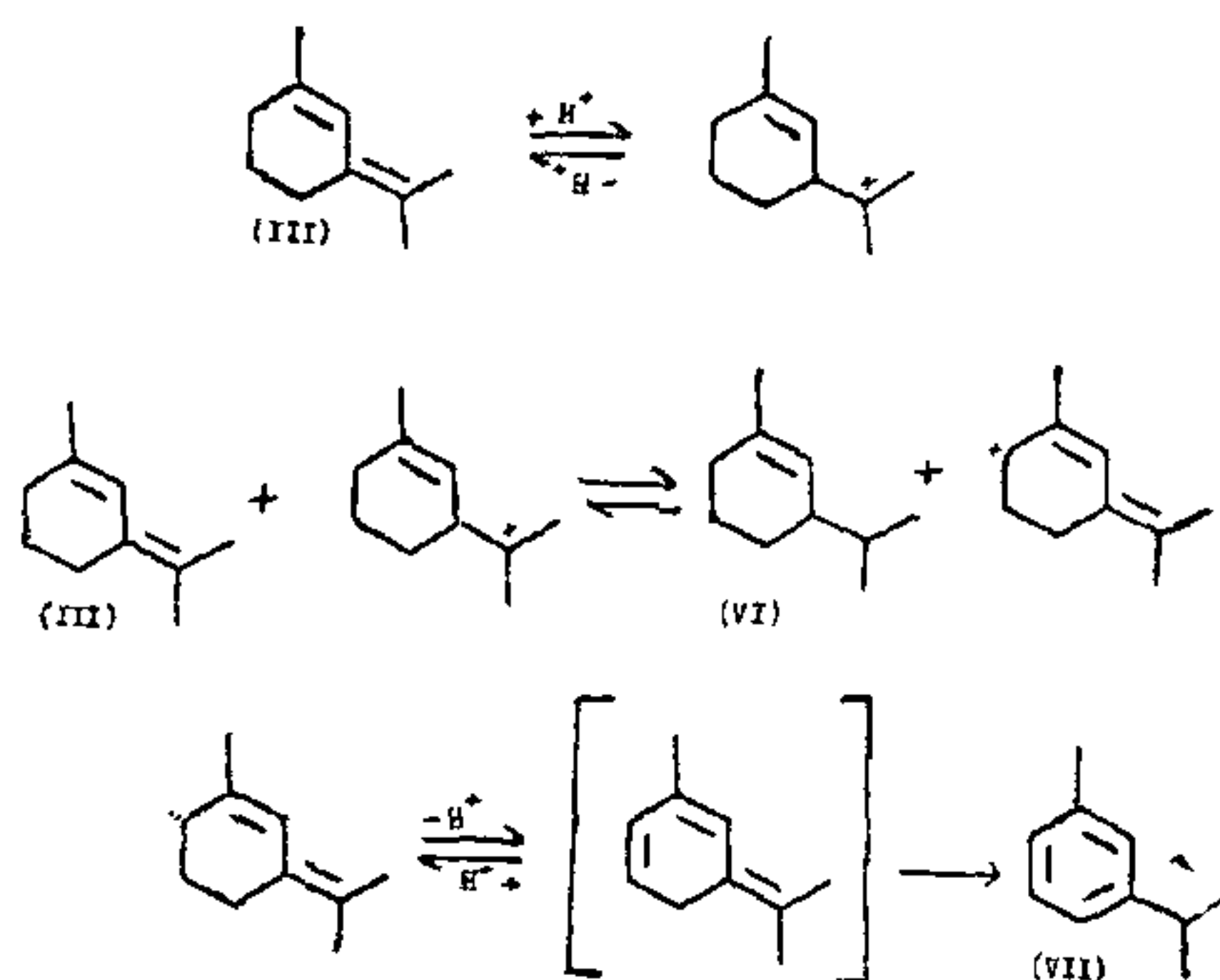
SCHEME I. Acid-catalysed rearrangement of *d*-sylvestrene.

m-Cymene (VII) and *m*-menth-1-ene (VI) may be generated through H⁺ induced disproportionation of *m*-menthadienes. We advance tentative Scheme II, with sylveterpinolene (III) as an example.

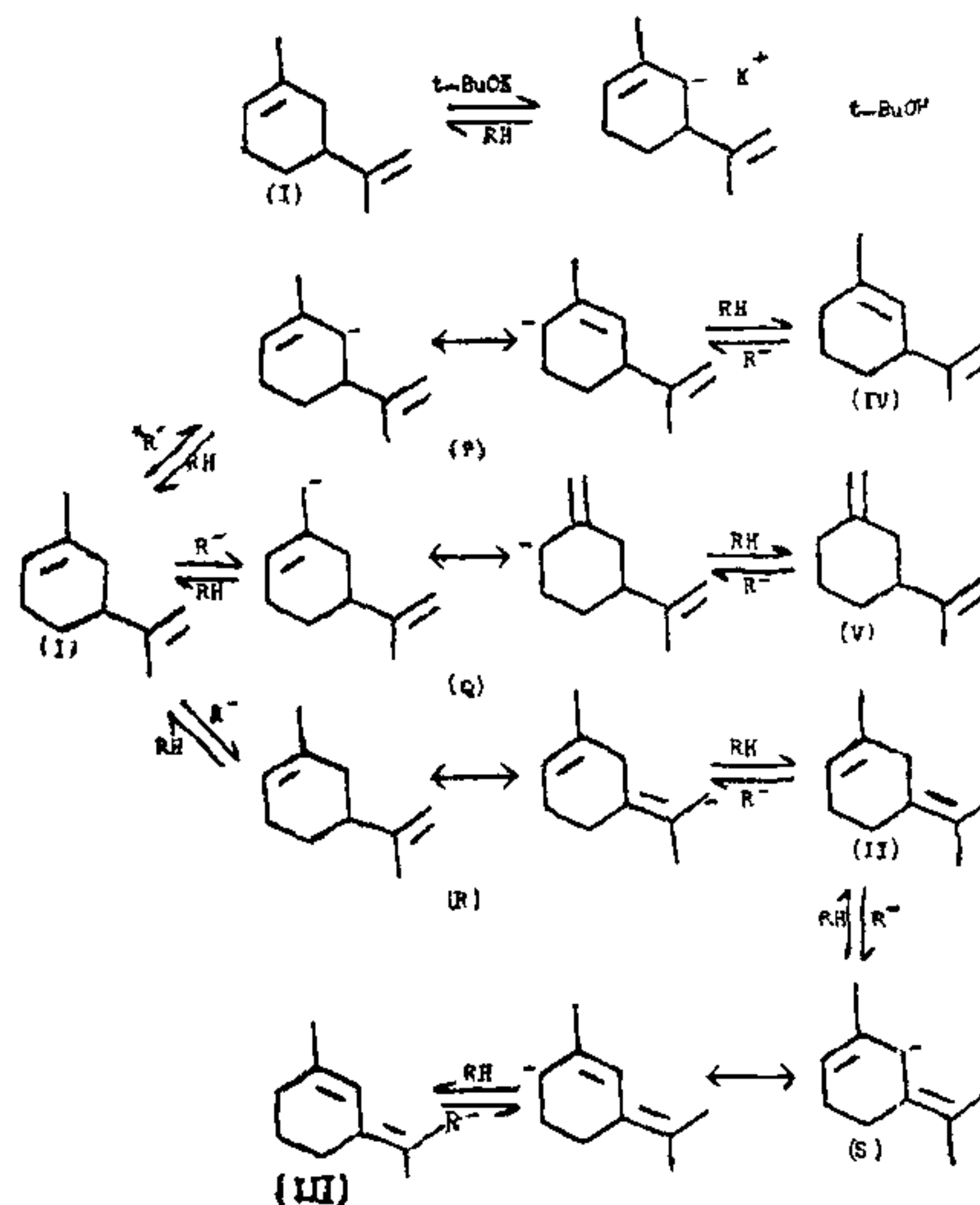
A mechanism involving allylic carbanion¹² may be invoked to accommodate the base-catalysed rearrangements of *m*-menthadienes as illustrated for *d*-sylvestrene (I) in Scheme III.

The allylic resonance hybrids (P), (Q), (R) and the biallylic carbanion (S) are the probable pre-

cursors of the isomers (IV), (V), (II) and (III) respectively.



SCHEME II. Disproportionation of sylveterpinolene.



SCHEME III. Base-catalysed rearrangement of *d*-sylvestrene.

*R⁻ represents a *m*-menthadienyl (C₁₀H₁₆)⁻ anion, K⁺ is omitted.

EXPERIMENTAL

For general experimental details see Part XXXVII¹³.

Materials.—Hydrocarbons (I), (II) and (III) were prepared by routes previously described^{1,2}.

Procedure.—The *m*-menthadienes were reacted with trichloroacetic acid and potassium *t*-butoxide as for (+)-limonene⁴ and car-3-ene¹⁴ respectively.

The catalysates were analysed by t.l.c., g.l.c., n.m.r. and chemical methods (Table I).

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1. Johnny, K. P. and Verghese, J., *Indian J. Chem.*, 1972, 10, 792.
2. Muraleedharan, N. V. and Verghese, J., *J. Indian Chem. Soc.*, 1972, 49, 291.
3. Bardyshev, I. I. et al., *Zhur. org. Khim.*, 1971, 7 (12), 2519.
4. Ipatieff, V. N. et al., *J. Amer. Chem. Soc.*, 1945, 67, 694.
5. Sheton, B. et al., *J. Org. Chem.*, 1968, 33, 221.

6. Bates, R. B. et al., *Ibid.*, 1969, 34, 2615.
7. Wallach, O., *Annalen*, 1887, 239, 1.
8. Brown, H. C., *J. Org. Chem.*, 1957, 22, 439.
9. Yamaguchi, T. et al., *Chem. Ind.*, 1961, p. 759.
10. Prahalada, J. R., *J. Sci. & Ind. Res.*, India, 1968, 27, 219.
11. Verghese, J., *Sympine, Seminar on the Role of Pine Resin in the Economic and Industrial Development of India*, 1971, DDD 1.
12. Pines, H. and Eschinazi, H. E., *J. Amer. Chem. Soc.*, 1955, 77, 6314.
13. Saraswathi, G. N. et al., *Indian J. Chem.*, 1974, 6, 561.
14. Acharya, S. P. and Brown, H. C., *J. Amer. Chem. Soc.*, 1967, 89, 1925.
15. Smith, M. E., *Ibid.*, 1921, 43, 1921.

EFFECT OF CROP SEQUENCE ON *ASPERGILLUS FLAVUS* INFESTATION AND AFLATOXIN ACCUMULATION IN GROUNDNUT (*ARACHIS HYPOGAEA* L.)

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A *SPERGILLUS FLAVUS* is an ubiquitous fungus known to invade a variety of agricultural and food commodities and produce a group of toxic metabolites known as aflatoxins, which are highly carcinogenic. Only a few strains are toxin producing and groundnut is said to be one of the best substrates for aflatoxin production^{1,4}. This fungus may invade groundnut pods while developing in the soil or after the harvest and subsequent storage^{1,7,8}.

Crop rotation is said to be one of the most beneficial agronomic practices to control certain diseases and also to regain soil fertility. Pettit and Taber (1968) found that groundnut harvested from lands planted with the same crop during the previous season also was more highly infested with fungi and contained more aflatoxins than groundnut raised on lands planted with rye, oats, melons or potatoes as the previous crop. Joffe and Lisker (1970) also found high fungal infestation to groundnut kernels in fields previously sown with groundnut than non-groundnut soils.

The objective of present investigation is to examine the effect of crop sequence on *A. flavus* and other fungal populations in soil, rhizosphere and geocarposphere, shells and kernels at various stages of crop development and also aflatoxin content at harvesting period.

Field plots (approx. 7 × 12 m in size) with different crop sequence history were selected near

S.V. University Campus, Tirupati (A.P.). The plots had the following crop sequence in *Kharif* and *Rabi* since three years. Plots with vegetable crop (brinjal, chilli, tomato and mesta as mixed crops) in *Kharif* and groundnut in *Rabi*; rice in *Kharif* and groundnut in *Rabi* and groundnut in both seasons. In each case three replicated plots were maintained and cultivated under similar agronomic practices. Fungal populations, pod infestation and aflatoxin accumulation were studied in late *Rabi* season (February–May) of 1972 and 1973. The soils are of red sandy type, low in organic matter content and colloidal content¹².

For the estimation of fungal populations, ten plants were pulled up from different regions of each replicated plot. The plants and also the soil in between the rows (control soil) were brought to the laboratory in polythene bags. The rhizosphere and geocarposphere mycofloras were estimated according to the method of Rao (1962) and Joffe (1969) respectively. Shell and kernel infestation was examined by the method of McDonald (1970). At the time of harvest about 15,000 pods from each replicated plot were collected and graded into (1) "Undamaged pods" (without any kind of damage) and (2) "damaged pods" (rotted, insect-bored, injured, etc.). Aflatoxins were estimated in both undamaged pods and damaged pods by the method of Pons et al. (1966) and confirmed by bioassay using *Bacillus maqeterium* (NRRL 1368) and *B. brevis* (NRRL 1874) following the method of Burmeister and Hesseltine (1966).

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