The Absolute Configuration of Trisubstituted Allenes Studied by Partial Hydrogenation

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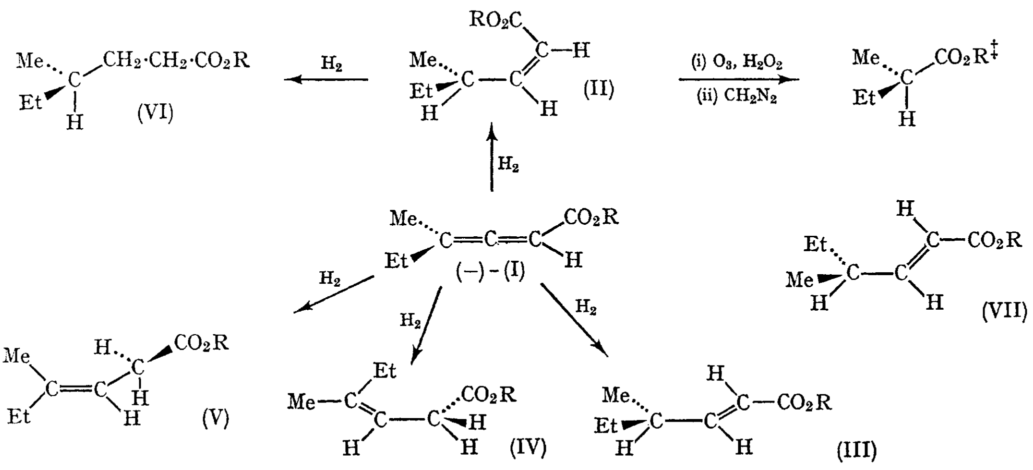
CONSIDERATIONS of catalyst hindrance and *cis*-addition of hydrogen from a catalyst (Pd–$BaSO_4$) suggest that semi-hydrogenation of a suitably substituted optically active allene should proceed with conversion of permolecular asymmetry into atomic asymmetry and lead to a simple method for determining absolute configuration. The hydrogenation of (±)-4-methylhexa-2,3-dienoic acid[1] and its methyl ester were studied (Figure 1). Selectivity was reasonable but hydrogenation gave much more alk-3-enoic product than did buta-2,3-dienoic and 2-methylbuta-2,3-dienoic acid and ester examined by us elsewhere.[2] This indicates attack on the 2,3-double bond in the orientations for (I) with Me or Et pointing into the catalyst, or else attack on the 3,4-double bond from the side with H pointing into the catalyst, followed by isomerisation *via* a π-allyl intermediate (Table 1). The expected 3,4-hydrogenation product from the latter orientation, *cis*-2-enoic acid (II), was present, but, surprisingly, *trans*-2-enoic acid (III), which would be produced by 3,4-hydrogenation in the



‡ Oxidation effected on enantiomer.

most hindered orientation, was present in similar amount. The possibility of *trans*-2-enoic acid (III) being produced by stereomutation of (II) or isomerisation from (IV) or (V) was, therefore, explored. 4-Methyl-[1-^{14}C]hex-*cis*-2-enoic acid or ester was hydrogenated together with the corresponding allene (I) and transference of radioactivity to the acid (III), separated by g.l.c., was followed. Preliminary experiments over the range 0—0·5 mol. hydrogen absorbed indicate that 98% of the acid (III; R = H) and 99% of the ester (III; R = Me) was being produced this way. Such extensive stereomutation during the 0—1 mol. absorption of hydrogen stage is unusual, though familiar enough during the 1—2 mol. stage.[2] Experiments with 4-methyl[1-^{14}C]hex-3-enoate showed that no 3,4 → 2,3-isomerisation occurred in the hydrogenation.

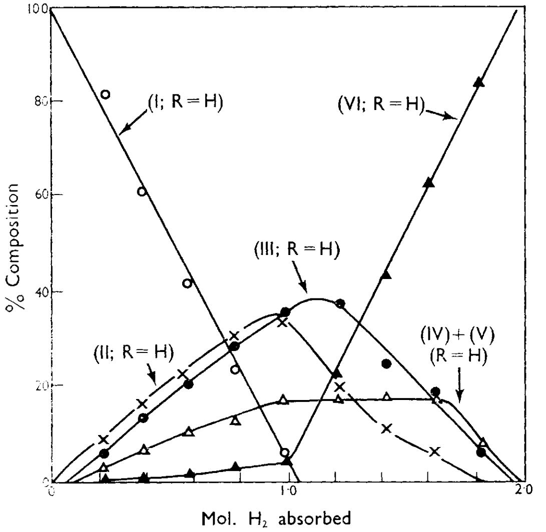


FIGURE. *Hydrogenation of 4-methylhexa-2,3-dienoic acid.*

The allene (±)-(I; R = H) was resolved with quinine to give (−)-(I; R = H), m.p. 45°, $[\alpha]_D^{24}$ $-36\cdot1° \pm 0\cdot2°$, and esterified to yield (−)-(I; R = Me), b.p. 70°/11 mm., n_D^{18} 1·4704, $[\alpha]_D^{24}$ $-29\cdot4° \pm 0\cdot1°$. Partly resolved (+)-(I; R = H), m.p. 35°, $[\alpha]_D^{24}$ $+21\cdot7° \pm 0\cdot2°$ was also obtained. Two active allenes were semi-hydrogenated and the products were isolated by preparative g.l.c.† with the results given in Table 1 and 2. The

TABLE 1. *Product analysis at the semi-hydrogenation point of allenes*

Allene	(I)	(II)	(III)	(IV) + (V)	(VI)	Sel.[a]
(±)-(I; R = H)	5	34·5	37·5	18·5	5·5%	0·90
(−)-(I; R = H)	7·5	30·5	34	20	8	0·85
(±)-(I; R = Me)	1	54	26·5	16	1	0·98
(−)-(I; R = Me)	0	56	22	17·5	2·5	0·97

[a] Sel. = Selectivity given by the ratio of % olefinic products to total % composition.

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† Preparative conditions: 20 ft. × $\frac{3}{8}$ in. aluminium column containing poly(ethyleneglycol succinate) (30%) on Chromosorb P: carrier gas N_2 (120 ml./min.) using stream-split flame ionisation detection. Analytical conditions: 10 ft. × $\frac{1}{8}$ in. stainless steel column containing P.E.G.S. (10%) on silanised Chromosorb W: carrier gas N_2 (25ml./)min. (all separations as methyl esters).

TABLE 2. *Rotations of products isolated (g.l.c.) from the semi-hydrogenation of optically active allenes*

Allene	(II)	(III)	(IV) + (V)	(VI)
(−)-(I; R = Me)[a]	$[\alpha]_D$ −9·8° ± 0·2°	−5·0° ± 0·2°	0°	−2·8° ± 0·4°
(+)-(I; R = H)[b,c]	$[\alpha]_D$ +5·5° ± 0·2°	+1·8° ± 0·3°	0°	+1·4° ± 0·5°

[a] $[\alpha]_D$ −29·4° ± 0·1°; [b] $[\alpha]_D$ + 21·7° ± 0·2°; [c] rotation as methyl esters.

separated (−)-(II; R = Me), on hydrogenation gave (−)-methyl 4-methylhexanoate $[\alpha]_D^{21}$ −7·4° ±0·2° (lit.[3] $[\alpha]_D^{25}$ + 8·03° for enantiomer: 96% retention of configuration). The absolute configuration of (−)-(VI) is known[3] to be (*R*) and, accepting *cis*-addition from the catalyst to the least hindered side,[4,5] the absolute configuration of (−)-(I) is thus (*R*). In confirmation, oxidation of (+)-(II; R = Me), and esterification, gave with some racemisation, (+)-(*S*)-methyl 2-methylbutyrate[6,7] $[\alpha]_D^{23}$ + 5·1° (lit.[7] $[\alpha]_D^{25}$ + 23·9°.

Had the *trans*-2-acid been produced by direct 3,4-hydrogenation of the (−)-(I) in its most hindered orientation, it would have configuration (VII) *i.e.*, be the enantiomer of (III). In fact, (+)-*trans*-(III; R = Me) from the partial hydrogenation gave, on oxidation and conversion into methyl 2-methylbutyrate, a product $[\alpha]_D^{24}$ +2·0° ± 0·5. The sign agrees with the finding that most of the *trans*-2-component arises by stereomutation from (II), though some racemisation has occurred in this process.

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