## The Chemistry of Terpenes. Part I. Hydrogenation of the Pinenes and the Carenes \*

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Conditions have been established for the catalytic hydrogenation of (+)- $\alpha$ -pinene to give over 98% of (+)-*cis*-pinane. Modification of the reaction conditions leads to the formation of over 50% *trans*-pinane. Conditions have also been established for the hydrogenation of (+)-car-3-ene giving over 98% of (-)-*cis*-carane. *Trans*-carane has not yet been obtained, but under appropriate conditions (+)-car-3-ene affords quantitative yields of 1,1,4-trimethylcycloheptane, suggested intermediates in the formation of which have been isolated, including (+)-car-2-ene.

The availability of the techniques of chromatography, particularly preparative gas-liquid chromatography (g.l.c.), and spectroscopy in its various forms prompted us to reinvestigate the chemistry of some simple terpenes, which are very suitable systems for examination by the techniques mentioned. Our first investigations were concerned with the catalytic hydrogenation of (+)- $\alpha$ -pinene, and from thence we extended our investigations to the carenes. In both cases novel results were obtained.

 $(+)-\alpha$ -Pinene (I) was difficult to obtain in an optically pure condition. Our work was therefore carried out with chromatographically pure hydrocarbon of ca. 75% optical purity.<sup>1</sup> (-)- $\beta$ -Pinene (II) was chromatographically, and probably optically, pure.<sup>2</sup> For comparison, (-)-cis-pinane (III) was prepared by hydrogenation of (-)- $\beta$ -pinene over palladised charcoal and isolated by preparative g.l.c. (+)-trans-Pinane (IV) was obtained as the principal product of thermal hydroboronation of (+)- $\alpha$ -pinene followed by reductive cleavage of the borane. ef. 3 The pure trans isomer was separated, by preparative g.l.c., from the mixture, which consisted of approximately 96% trans- and 4%cis-pinanes and other minor products. As previously reported <sup>3</sup> we found that the nuclear magnetic resonance (n.m.r.) spectra of the two isomers were different, the  $C_9$  and  $C_{10}$  methyl protons being deshielded (ca. 0.18 p.p.m.) in the cis-compound.

Non-catalytic reductions in general gave mainly *trans*-pinane. Thus lithium aluminium hydride reduction of (-)- $\beta$ -pinene was shown (g.l.c.) to give a *trans/cis* pinane ratio of 89/11, but (+)- $\alpha$ -pinene was not affected

\* This work was described at a symposium on the chemistry of terpenes held at Poona in June 1965. Cf. Chem. Comm., 1965, 254.

<sup>1</sup> J. L. Simonsen, "The Terpenes," vol. II, Cambridge Univ. Press, 1949, p. 132.

<sup>2</sup> J. L. Simonsen, ref. 1, p. 198.

by this reagent. Kishner-Wolff reduction of (+)-isopinocamphone (IIIa; R = =0) gave a poor yield of pinanes consisting of 87% (g.l.c.) of the *trans*-isomer.



It is of interest that lithium in ethylamine at room temperature reduced both (+)- $\alpha$ - and (-)- $\beta$ -pinene to a mixture shown by g.l.c. to consist of 56—57% cis- and 44—43% trans-pinane.

(+)- $\alpha$ -Pinene was hydrogenated using a variety of different temperatures, hydrogen pressures, catalysts, and solvents, the products were examined by g.l.c. and the percentage of *cis*- and *trans*-isomers estimated from peak areas by comparison with authentic compounds. Products other than pinanes were not formed in excess of 5% at temperatures below 130°. As can be seen from Table 1, a fairly large variation in the *cis/trans*-pinane ratio is possible even at room temperature and below. Previously yields of 80 or 90% of *cis*-pinane have been obtained <sup>3-5</sup> when platinum and palladium were the catalysts. We have found that some variation in the *cis/trans* ratio occurs when different batches of palladised charcoal are used, in particular the more active commercial catalyst favours formation of *trans*-isomer.

Table 1 also shows that the bulky gem-dimethyl <sup>3</sup> H. C. Brown and G. Zweifel, J. Amer. Chem. Soc., 1964, 86, 394

394.
<sup>4</sup> C. L. Arcus, L. A. Cort, and T. J. Howard, J. Chem. Soc., 1960, 1195.
<sup>5</sup> E. E. Van Tamelen and R. J. Timmons, J. Amer. Chem.

<sup>•</sup> E. E. Van Tamelen and R. J. Timmons, J. Amer. Chem. Soc., 1962, 84, 1067.

TABLE 1 Catalytic hydrogenations of (+)- $\alpha$ -pinene

		2	Ç	( · / I		
				% Pir	% Pinane	
		Press.		(+)cis- (IIIa;	(+)trans-	
Catalyst	Temp.	(atm.)	Solvent	R = H	(IV)	
5% Pt/C	$20^{\circ}$	100	EtOH	98.5	1.5	
5% Pt/C	20	<b>30</b>	EtOH	97.5	$2 \cdot 5$	
PtO <sub>2</sub>	<b>20</b>	1	EtOH	93.5	6.5	
5% Pt/C	20	1	EtOH	90.0	10.0	
5% Pd/C	0	1	EtOH	80.0	20.0	
5% Pd/C	20	1	Propionic acid	74.0	26.0	
5% Pd/C	20	1	Acetic acid	73.0	$27 \cdot 0$	
5% Pd/C	<b>20</b>	1	EtOH	65.0	$35 \cdot 0$	
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group inhibits absorption of the  $\beta$ -face of the pinene on the surface of the catalyst. Normal four centre hydrogenation therefore takes place preferentially from the  $\alpha$ -face of the molecule giving *cis*-pinane. This is particularly the case over platinum, and when the pressure of hydrogen is high. Under these conditions the catalyst is saturated and the reaction must be rapid. In the final stage of the non-catalytic reductions described above, however, the bulkiness of the gemdimethyl bridge favours displacement of the 10-methyl group or its derivative to the trans arrangement with respect to the bridge. This is particularly so during thermal rearrangement of the boranes, where the effective volume of the 10-methyl group is greatly increased on becoming  $-CH_2 \cdot B \leq$ . Steric control is probably different in the lithium in ethylamine reduction, in which the important step is presumably the donation of hydrogen to a carbanion by the solvent.

$$\underbrace{\underbrace{}_{(I)}^{\mathsf{H}} \xrightarrow{\mathsf{BH}_{3}}}_{(I)} \left[ \underbrace{\underbrace{}_{\mathcal{H}_{2}}^{\mathsf{H},\mathsf{H}_{3}} \xrightarrow{\mathsf{H}_{2},\mathsf{CH}_{2},\mathsf{B}_{3}}}_{(IV)} \right] \rightarrow \underbrace{\underbrace{}_{\mathcal{H}_{2}}^{\mathsf{H},\mathsf{CH}_{3}}}_{(IV)}$$

In an effort to increase the proportion of *trans*-pinane produced by catalytic hydrogenation we studied the

TABLE	2
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Effect of temperature on the hydrogenation of  $(+)-\alpha$ pinene (I) in propionic acid using palladised charcoal as catalyst o/ T)

	% Pinanes				
Temp.	(+)-Cis- (IIIa; $R = H$ )	(+)- <i>Trans</i> - (IV)			
0°	80	20			
20	73.5	26.5			
52	64.5	35.5			
73	62.5	37.5			
89	55.5	44.5			
111	52.0	<b>48</b> ·0			
127	47.0	53.0			
138	48.5	51.5			

effect of increase of temperature on the reaction. Hydrogenations were carried out in propionic acid. The results of these experiments are given in Table 2.

<sup>6</sup> R. L. Burwell, B. K. Shim, and H. C. Rowlinson, J. Amer. Chem. Soc., 1957, 79, 5142.

 <sup>7</sup> R. L. Burwell, *Chem. Rev.*, 1957, **57**, 895.
 <sup>8</sup> R. P. Linstead, K. O. A. Michaelis, and S. L. S. Thomas, J. Chem. Soc., 1940, 1139.

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Several suggestions can be made to explain the increase in the proportion of trans-isomer with increase in temperature. (a) The cis-isomer might be isomerised by heat. This unlikely possibility can be excluded, since (+)-cis-pinane is unaffected under the conditions of the hydrogenation, and furthermore deuterium is not incorporated under these conditions. (b) Thermal deformation of the  $\alpha$ -pinene molecule might allow shift of equilibrium between  $\alpha$ - and  $\beta$ -face-absorbed species towards the latter. (c) At higher temperatures another mechanism employing a differently absorbed species cf. 6,7 might assume prominence so as to give trans-pinane by thermodynamic control of the reaction. We have not yet studied the mechanism of these reductions.

Above  $120^{\circ}$  small amounts (ca. 2%) of two further components were also formed in the hydrogenation reaction. In the absence of hydrogen, *i.e.*, when (+)- $\alpha$ pinene was refluxed over the catalyst, these minor products were formed in considerably increased amounts due to disproportionation. They were separated and purified by preparative g.l.c. and identifed as p-cymene and camphene. The relative proportions were  $\alpha$ -pinene (2.5%), *cis*-pinane (13%), *trans*-pinane (13%), p-cymene (46%), camphene (19.5%), cf. 8 and other components (6%).

Continuous analysis by g.l.c. of the hydrogenation of (+)- $\alpha$ -pinene in ethanol at room temperature and one atmosphere over palladised charcoal showed that no preliminary double bond isomerisation took place. However, when (-)- $\beta$ -pinene was the substrate there was rapid and complete isomerisation, with retention of configuration to the more stable  $\alpha$ -pinene as is shown in Figure 1. No isomerisation, however, took place in the absence of free hydrogen, which is in agreement with earlier work.9

The carenes have rigid molecules, and might be expected to behave like the pinenes on reduction. However, unlike the pinanes, *cis*- and *trans*-carane have not been adequately described.

(+)-Car-3-ene (V) was obtained in a chromatographically and ca. 90% optically 10 pure condition by preparative g.l.c. using a (+)-car-3-ene-rich fraction of a Baltic turpentine. Its physical characteristics are described in the Experimental section.

Initial hydrogenation experiments with (+)-car-3-ene carried out in ethanol at room temperature and one atmosphere pressure using commercial palladised charcoal (these conditions are referred to hereafter as "standard") showed that (-)-cis-carane (VI) and 1,1,4-trimethylcycloheptane (VII) were formed in about equal proportions (g.l.c.). The proportions, however, varied widely with reaction conditions. Thus over platinised charcoal at 100 atmospheres of hydrogen and at room temperature *cis*-carane was virtually (98%)the only product. We assign its structure on the basis

<sup>9</sup> F. Richter and W. Wolf, Ber., 1926, 59, 1733; cf. J. B. Bream, D. C. Eaton, and H. B. Henbest, J. Chem. Soc., 1957, 1974. <sup>10</sup> Y. R. Naves, Bull. Soc. chim. France, 1959, 554.



FIGURE 1 Percentage composition of reaction mixture during hydrogenation of (-)- $\beta$ -pinene (II)

of its n.m.r. spectrum, which showed absorption due to two cyclopropane protons ( $\tau$  9·2—9·8), one gem-dimethyl group ( $\tau$  9·07 and 9·02) and one ring methyl group ( $\tau$  9·18, J = 5.5 c./sec.) p.p.m., and by analogy with the formation of (+)-cis-pinane from (+)- $\alpha$ -pinene. Its physical properties were very similar to those of a compound tentatively described by Naves <sup>10</sup> as transcarane (VIII).



The uptake of hydrogen during the formation of (VI) and (VII) under standard conditions was equivalent to one mole per mole of (VI) and two moles per mole of (VII). At higher temperatures the change in proportions of the products was greater than was the case with the pinanes (see Table 3). Thus above 90° in propionic acid, two moles of hydrogen per mole of (+)-car-3-ene were absorbed and 1,1,4-trimethylcycloheptane was formed quantitatively. It was optically inactive, and its n.m.r. spectrum showed the presence of a gem-dimethyl group and one ring methyl but no cyclopropane protons. Its g.l.c. and other physical properties were identical with an authentic specimen prepared from eucarvone.<sup>11</sup>

Since in the absence of free hydrogen (+)-car-3-ene is unaffected by palladised charcoal in propionic acid at 95°, the formation of 1,1,4-trimethylcycloheptane (VII) must involve the cleavage of the internal cyclopropane ring bond by hydrogen. We found no evidence

## TABLE 3

Effect of temperature on the hydrogenation of (+)-car-3-ene in propionic acid using palladised charcoal as catalyst

Temp.	% cis-Carane	% 1,1,4-Trimethyl- cycloheptane
0°	35.5	64.5
8	33.0	67
<b>20</b>	26.0	74
33	18.5	81.5
<b>48</b>	7.0	93
61	$3 \cdot 0$	97
73	0	100
90	0	100
106	0	100
126	0	100

in the n.m.r. spectrum or during extensive g.l.c. analysis for the presence of *trans*-carane in this hydrogenation product, and therefore we conclude that it is not formed in the reaction.

Examination by g.l.c. of the course of the hydrogenation of (+)-car-3-ene, under standard conditions, showed that it rapidly equilibrates with (+)-car-2-ene (IX). This was isolated in a pure condition by chromatography on silica gel impregnated with silver nitrate, followed by preparative g.l.c. Its physical characteristics were in good agreement with those of (±)-car-2-ene.<sup>10</sup> The two isomers remain (60%  $\Delta^3$ - and 40%  $\Delta^2$ -) in equilibrium throughout the hydrogenation (Figure 2). No equilibration takes place in the absence of free hydrogen.





The identity of the (+)-car-2-ene was established by its infrared spectrum,<sup>10</sup> refractive index,<sup>10</sup> optical rotation,<sup>12</sup> its n.m.r. spectrum which showed only one olefinic proton, and its ultraviolet spectrum which showed

<sup>&</sup>lt;sup>11</sup> J. R. B. Campbell, A. M. Islam, and R. A. Raphael, *J. Chem. Soc.*, 1956, 4096.

<sup>&</sup>lt;sup>12</sup> R. Padmanabhan and S. K. K. Jatkar, J. Amer. Chem. Soc., 1935, **57**, 334.



FIGURE 3 Percentage composition of reaction mixture during hydrogenation of (+)-car-2-ene (IX) 3-ene. (VI) *cis*-Carane. (VII) 1,1,4-Trimethylcyclo-[(V) Car-3-ene. (VI) cis-Carane. heptane.]

Since the equilibration of these isomers does not involve the cyclopropane ring, the absolute configuration of (+)-car-2-ene (IX) is no longer in doubt.<sup>14</sup>

During the separation of (+)-car-2-ene by g.l.c. we isolated small amounts of 1,1,4-trimethylcyclohept-3-(X) <sup>15</sup> and 4-ene (XI). The last two compounds were, however, isolated in 25% yields from the mixture obtained when (+)-car-3-ene was refluxed over palladised charcoal without hydrogen. Other products of the latter reaction were *m*-cymene (20%) and *p*-cymene (30%). The trimethylcycloheptenes (X) and (XI) each absorbed one mole of hydrogen giving (g.l.c.) 1,1,4-trimethylcycloheptane, whilst their n.m.r. spectra showed absorption at  $\tau$  9.08 and 9.14 (6 protons, gem-dimethyl), 8.37 and 8.30 (3 protons, allylic methyl), and 4.70 and 4.73 (1 proton, olefinic) p.p.m., respectively. Each pure isomer was rapidly equilibrated over palladised charcoal by hydrogen to a mixture of the 3-ene (35%)and the 4-ene (65%). The individual structures are tentatively assigned on the basis of differences in the deshielding of (a), the gem dimethyl (b), the allylic methyl groups, the greater symmetry of the 4-ene (XI) as judged from the n.m.r. spectra, and by analogy with the equilibrium proportions of (+)- $\Delta^3$ -and (+)- $\Delta^2$ -carenes.

In view of the rapid formation of (+)-car-2-ene (IX) from (+)-car-3-ene (V) we believe that the former is a necessary precursor of 1,1,4-trimethylcycloheptane (VII) in the hydrogenation, under standard conditions, and at higher temperatures in propionic acid. (-)-cis-Carane (VI) is not an intermediate in this reaction since

<sup>13</sup> A. I. Scott, "Interpretation of the Ultraviolet Spectra of Natural Products," Pergamon Press, 1964, p. 49.
 <sup>14</sup> A. J. Birch, Ann. Reports, 1950, 47, 193.

it is unaffected by the conditions which quantitatively convert (+)-car-3-ene to 1,1,4-trimethylcycloheptane. Moreover, detailed analysis by g.l.c. of the early part of the hydrogenation, under standard conditions, of pure (+)-car-3-ene showed that before much (+)-car-2-ene had been produced (-)-cis-carane was the predominant hydrogenation product. However, as (+)-car-2-ene accumulated, 1,1,4-trimethylcycloheptane became the predominant hydrogenation product. When (+)-car-2-ene was hydrogenated, 1,1,4-trimethylcycloheptane was always the predominant hydrogenation product, but it had greater predominance before (+)-car-3-ene was formed in appreciable quantities.



These facts suggest that in the formation of 1,1,4-trimethylcycloheptane, 1,4-addition of hydrogen to the conjugated system of car-2-ene occurs, giving 1,1,4-trimethylcyclohept-2-ene (XII), which is rapidly isomerised to the more stable 1,1,4-trimethylcyclohept-3- and 4-enes, which are then further reduced. No seven-membered cyclic dienes have been detected in our experiments even after disproportionation of (+)-car-3-ene.

## EXPERIMENTAL

General Experimental Conditions.-Melting points were uncorrected. Infrared spectra were measured on a Perkin-Elmer 137 Infracord spectrophotometer with the exception of those of compounds (III), (IV), (VI,) and (VII), which were recorded on a Hilger H 800 spectrophotometer; ultraviolet spectra were measured on a Unicam S.P. 500 spectrophotometer. N.m.r. spectra were recorded on a Perkin-Elmer R.10 instrument at 60 megacycles per second using tetramethylsilane as an internal standard; the solvent was carbon tetrachloride. Palladised charcoal (5%) and platinised charcoal (5%) were supplied by Johnson Matthey & Co. Ltd.; 10% palladised charcoal was prepared by the normal laboratory method.<sup>16</sup> Analytical g.l.c. was carried out on an Aerograph model 600 apparatus; columns are referred to as follows: (A), 3 metre, 20% squalene on Chromosorb W; (B), 3 metre, 20% Castorwax on Chromosorb W; (C), 3 metre, 20% S.A.I.B. on Chromosorb W, and (D), 3 metre, 20% Apiezon on Chromosorb W as support. Preparative g.l.c. was carried out with an Aerograph Autoprep model A.700 apparatus; columns are referred to as (E), 6 metre, 30% Apiezon on Chromosorb W, or (F), 6 metre, 30% Castorwax on Chromosorb W.

<sup>15</sup> H. Barbier, *Helv. Chim. Acta*, 1940, 23, 1477.
<sup>16</sup> A. Vogel, "Practical Organic Chemistry," Longmans, 1961, p. 950.

(-)-cis-Pinane (III).--(-)-β-Pinene (II),  $n_{\rm D}^{20}$  1·4784,  $[\alpha]_{\rm D}^{20} - 21^{\circ}$  (30 g.) was hydrogenated in ethanol (100 c.c.) over 10% palladised charcoal (3 g.) at 20° and 1 atm. for 14 hr. G.l.c. on column (B) at 121° indicated a *cis/trans* pinane ratio of 80/20. Preparative g.l.c. on column (E) at 125° gave pure (-)-*cis*-pinane (III),  $n_{\rm D}^{20}$  1·4624,  $[\alpha]_{\rm D}^{20}$ -19·5°,  $v_{\rm max}$  (liq. film) 2900, 1473,\* 1466, 1458, 1452,\* 1380, 1371, 1363, 1351, 1343, 1320, 1275, 1262, 1226, 1160, 1117, 1098, 1083, 1040, 1025, 1000, 980, 951, 936, 920, 870, 857, 810, 780, and 754 cm.<sup>-1</sup> (\* denotes shoulder),  $\tau$ 8·98 (doublet,  $J = 7\cdot2$  c./sec., intensity 3, C<sub>10</sub> methyl), 8·97 (singlet, intensity 3, C<sub>9</sub> methyl) and 8·80 (singlet, intensity 3, C<sub>8</sub> methyl) p.p.m. (Found: C, 87·1; H, 12·8. Calc. for C<sub>10</sub>H<sub>18</sub>; C, 86·9; H, 13·1%).

(+)-trans-*Pinane* (IV).--(+)- $\alpha$ -Pinene (I),  $n_{\rm D}^{20}$  1.4661,  $[\alpha]_{\rm p}^{20} + 23.0^{\circ} (24 \text{ g.})$  was stirred, under nitrogen, in diglyme (80 c.c., redistilled over  $LiAlH_4$ ) with freshly ground sodium borohydride (3 g.). Redistilled boron trifluoride etherate (13.5 g.) in diglyme (30 c.c.) was added over 20 min., the mixture was stirred for 2 hr. at  $20^{\circ}$  and then heated under reflux for 6.5 hr. under nitrogen. After cooling, glycerol (7 c.c.) and propionic acid (21 c.c.) were added to the pink residue, and the mixture was again heated under reflux for 7 hr. under nitrogen. On cooling, the mixture was treated with 10N-sodium hydroxide until alkaline, and the upper layer was washed three times with water, dried, and distilled. The fractions distilling between 90° and 180°, containing crude pinanes (10.0 g.), showed amongst other components a cis/trans pinane ratio of 4/96 on g.l.c. on column (A) at 100°. Preparative g.l.c. on column (E) at 125° gave (+)-*trans*-pinane (IV),  $n_{\rm D}^{20}$  1.4615,  $[\alpha]_{\rm D}^{20}$  + 5.9° (c 3.6),  $v_{\rm max}$ . (liq. film), 2910, 1475, 1458, 1451,\* 1380, 1371, 1365, 1318, 1298, 1264, 1232, 1223, 1200, 1161, 1152,\* 1081, 1051, 1038, 1004, 946, 937, 918, 887, 869, 851, 816, and 771 cm.<sup>-1</sup> (\* denotes shoulder),  $\tau$  9.15 (doublet, J = 7 c./sec., intensity 3, C10 methyl), 9.17 (singlet, intensity 3, C9 methyl) and 8.80 (singlet, intensity 3, C<sub>8</sub> methyl) p.p.m. (Found: C, 86.8; H, 13.0. Calc. for C<sub>10</sub>H<sub>18</sub>: C, 86.9; H, 13.1%).

Lithium Aluminium Hydride Reduction of (-)- $\beta$ -Pinene (II).—(-)- $\beta$ -Pinene (13.6 g.) was kept at 150° with lithium aluminium hydride (2.0 g.) under nitrogen for 48 hr. Cautious treatment of the cooled mixture with water followed by ether extraction yielded a colourless oil (9.0 g.). G.1.c. on column (A) at 100° showed the product to contain 95% of pinanes with a *cis/trans* pinane ratio of 11/89.

Reduction of (+)- $\alpha$ -Pinene (I) and (-)- $\beta$ -Pinene (II) with Lithium in Ethylamine.—(+)- $\alpha$ -Pinene (21.0 g.) was added dropwise with stirring to a solution of lithium (4.0 g.) in dry ethylamine (300 c.c.). The mixture was stirred for 17 hr. and more lithium (2.0 g.) was then added. After stirring for a further 31 hr. undissolved lithium was removed mechanically, ammonium chloride (15.0 g.) added, and water was cautiously dropped in. The mixture was extracted with ether, the ether layer was washed with water (4 × 80 c.c.), dried, and the solvent was removed by evaporation, giving a yellow oil (18.5 g.). G.I.c. on column (A) at 100° showed the product to consist of 98% pinanes with a *cis/trans* ratio of 56/44. Reduction of (--)- $\beta$ -pinene (8.6 g.) in a similar manner gave a *cis/trans* pinane ratio of 57/43.

Kishner-Wolff Reduction of (+)-Isopinocamphone (IIIa; R = O).--(+)-Isopinocamphone<sup>17</sup> (7.5 g.) was heated at 155° for 20 hr. with 100% hydrazine hydrate (5.0 g.). Ether extraction and evaporation of solvent from the dried solution gave the crude hydrazone. Sodium (0.6 g.) View Article Online in ethanol (8 c.c.) was added, and the temperature was raised to  $150^{\circ}$  and maintained there for 15 hr. Steam distillation gave an oil which, after drying, was distilled over sodium, affording the crude pinanes (1·2 g.). G.1.c. on column (A) at 100° showed the product to contain 80% pinanes with a *cis/trans* ratio of 13/87.

Hydrogenation of (+)- $\alpha$ -Pinene (I) using Various Catalysts, Solvents, and Temperatures (see Tables 1 and 2).—In each case (+)- $\alpha$ -pinene (200 mg.) was hydrogenated in solvent (5 c.c.) using 40 mg. of catalyst. For hydrogenations at elevated temperatures, the hydrogenation flask was fully immersed in an oil bath kept at the required temperature for 5 min. before stirring was commenced. For reductions at 112°, hydrogen uptake and n.m.r. analysis of products revealed only *cis*- and *trans*-pinanes.

(+)-Cis-Pinane (100 mg.), stirred in the presence of hydrogen over 10% palladised charcoal (40 mg.) in propionic acid (1 c.c.) at 135°, was unaffected after 1 hr. In the presence of a 10-fold excess of 20% deuterium in hydrogen at 130° over 10% palladised charcoal no deutero pinane was formed after 30 min. [Mass spectrum, by courtesy of Dr. R. T. Aplin showed no (<2%) deuterium in recovered *cis*-pinane.]

For the high pressure hydrogenations, (+)- $\alpha$ -pinene  $(1\cdot 0 \text{ g.})$  in ethanol (30 c.c.) was hydrogenated in an autoclave, over 5% platinised charcoal  $(0\cdot 2 \text{ g.})$  at room temperature and 30 and 100 atm. The *cis/trans* pinane ratios of the products (in ether) were estimated by g.l.c. on column (A) at 100°.

Continuous Analysis of the Mixtures during the Hydrogenation of Pinenes and Carenes (see Figures 1, 2, and 3).--(-)- $\beta$ -Pinene (II) (200 mg.) in ethanol (5 c.c.) was stirred with 5% palladised charcoal (100 mg.) at  $20^{\circ}$  and 1 atm. of hydrogen. After 5 c.c. of hydrogen had been taken up a small sample (ca. 0.1 c.c.) was withdrawn, filtered from catalyst, and analysed directly on g.l.c. column (A) at 100°. Further samples were analysed at 5 c.c. intervals until no more hydrogen was taken up. The same procedure was used for  $(+)-\alpha$ -pinene (I), (+)-car-3-ene (V), and (+)-car-2-ene (IX). For the last two compounds, the experiments were repeated over the first quarter of the reaction, when samples were taken after the uptake of successive 1 c.c. of hydrogen. G.l.c. analysis was performed on column (B) at 100°. Starting with (+)-car-3-ene (V), cis-carane (VI) forms 70% of the saturated products after 4% reaction, but starting with (+)-car-2-ene (IX), 1,1,4-trimethylcycloheptane (VII) forms 65% of the saturated components after 4% reaction. No isomerisation of starting materials (V) or (IX) takes place in the absence of gaseous hydrogen.

Conversion of (-)- $\beta$ -Pinene to Optically Pure (-)- $\alpha$ -Pinene.-(-)- $\beta$ -Pinene,  $[\alpha]_{D}^{20} - 21^{\circ}$  (5 c.c.), in ether (20 c.c.) was stirred with 10% palladised charcoal under hydrogen (1 atm.) until 20 c.c. of gas had been absorbed. The product consisted of 95%  $\alpha$ -pinene by g.l.c. on column (A) at 100°. Preparative g.l.c. on column (E) at 130° gave pure (-)- $\alpha$ -pinene,  $n_{D}^{20}$  1·4662,  $[\alpha]_{D}^{20} - 51\cdot2^{\circ}$ .

Disproportionation of  $(+)-\alpha$ -Pinene.— $(+)-\alpha$ -Pinene (40 c.c.) was heated under reflux with 10% palladised charcoal (2.0 g.) for 36 hr. G.l.c. analysis on column (A) at 100° indicated the following 5 components in order of increasing retention times,  $\alpha$ -pinene (2.5%), camphene (19.5%), transpinane (IV) (13%), cis-pinane (III) (13%), p-cymene (46%),

<sup>17</sup> H. C. Brown and C. P. Garg, *J. Amer. Chem. Soc.*, 1961, **83**, 2952.

and other components (6%). Preparative g.l.c. on column (E) at 130° gave (a), camphene (semi-solid),  $\nu_{max}$  (liq. film) 3030, 2915, 1770, 1667, 1481,\* 1449, 1379, 1353, 1299, 1198, 1156, 1130, 1105, 1087, 1033, 877, 805, 758, and 744 cm.<sup>-1</sup>, identical with authentic camphene, unresolved from authentic camphene when examined on g.l.c. columns (A), (B), and (C), at 100°, 95°, and 120°, respectively (Found: C, 88.1; H, 12.3. Calc. for  $C_{10}H_{16}$ : C, 88.2; H, 11.8%), and (b), p-cymene,  $n_{\rm p}^{22\cdot5}$  1·4891,  $\lambda_{\rm max.}$  (EtOH) 2735, 2675, 2650, and 2600 Å (log  $\varepsilon 2\cdot53$ , 2·49, 2·49, and 2·41, respectively, v<sub>max.</sub> (liq. film) 2899, 1887, 1786, 1645, 1513, 1460, 1408,\* 1377, 1359, 1333,\* 1299, 1274, 1206, 1103, 1053, 1038,\* 1017, 933, 813, and 717 cm.<sup>-1</sup> (\*denotes shoulder), identical with authentic p-cymene. It was unresolved from authentic p-cymene on g.l.c. on the columns used for camphene (Found: C, 89.5; H, 10.6. Calc. for C<sub>10</sub>H<sub>14</sub>: C, 89.5; H, 10.5%).

(+)-Car-3-ene (V).—Crude (+)-car-3-ene,  $[\alpha]_{D}^{20} + 12 \cdot 1^{\circ}$ , from carene-rich fractions of Baltic turpentine, was purified by preparative g.l.c. on column (E) at 115°, and then had  $\begin{array}{c} \begin{array}{c} \text{By preparative grant of grant of$ and 709 cm.<sup>-1</sup>,  $\tau$  9.15–9.45 (multiplet, cyclopropane protons), 9.24 (singlet, C8 or C9 methyl), 8.97 (singlet,  $C_8$  or  $C_9$  methyl) 8.40 (multiplet, allylic methyl), and 4.75 (singlet, olefinic proton) p.p.m.

Hydrogenation of (+)-Car-3-ene (V) under Standard Conditions.--(+)-Car-3-ene (V) (102 mg.) was hydrogenated in ethanol (5 c.c.) over 5% palladised charcoal (52 mg.) at 20° and 1 atm. The hydrogen uptake (27.0 c.c.) corresponded to 1.5 moles per mole of carene. G.l.c. analysis on column (A) at  $100^{\circ}$  showed that the proportions of *cis*carane (VI) to 1,1,4-trimethylcycloheptane (VII) were 49/51. The experiment was repeated on a larger scale with (+)-car-3-ene (2.8 c.c.). The hydrogenation products, isolated by preparative g.l.c. on column (F) at 115°, showed n.m.r. absorption at 7 9.13 [singlet, gem-dimethyl of 1,1,4-trimethylcycloheptane (VII)], 9.08 [singlet, C<sub>9</sub> methyl of ciscarane (VI)], and 9.03 [singlet, C<sub>8</sub> methyl of cis-carane (VI)] p.p.m.

Hydrogenation of (+)-Car-3-ene (V) at Various Temperatures (see Table 3).--(+)-Car-3-ene (V) (100 mg.) in propionic acid (5 c.c.) was hydrogenated at 1 atm. over 5% palladised charcoal (50 mg.) at temperatures ranging from 0 to 141°. The hydrogenation flask was immersed in an oil-bath at the requisite temperature for 5 min. before stirring began. Reaction times varied from several hours (below  $20^{\circ}$ ) to about 5 min. (above  $100^{\circ}$ ). Analyses of the products in ether were performed by g.l.c. on column (A) at 100°. At 110°, (+)-car-3-ene (100 mg.) took up 32.5 c.c. of hydrogen, corresponding to 1.9 moles per mole of carene. At 116° in the absence of hydrogen but in propionic acid (5 c.c.), and with 5% palladised charcoal (50 mg.), (+)-car-3-ene was unaffected (g.l.c., mixture with starting material) after 1.5 hr.

1,1,4-Trimethylcycloheptane (VII).--(+)-Car-3-ene (V),  $n_{\rm D}^{20}$  1.4726,  $[\alpha]_{\rm D}^{20}$  +15.4° (2.0 g.) was hydrogenated in propionic acid (30 c.c.) at  $96^{\circ}$  over 5% palladised charcoal at atmospheric pressure. The mixture was filtered from catalyst, dissolved in ether (50 c.c.), and washed repeatedly with 10% sodium hydroxide and then water. After drying, the ether was removed on a water-bath and the yellow residue (2.0 g.) was purified by preparative g.l.c. on column (E) at  $120^{\circ}$ . The purified cycloheptane (VII) gave a single peak when analysed on columns (A), (B), and (C) by g.l.c.

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view Article Online and gave  $n_{\rm D}^{20}$  1·4414,  $\nu_{\rm max}$  (liq. film) 3166, 2938,\* 2908, 2850, 2700, 2667,\* 1460, 1440,\* 1385, 1375, 1363, 1290, 1256, 1230, 1217, 1183, 1142, 1100, 1080, 1052, 1040,\* 1002, 985, 963,\* 951, 934, 893, 884, 817,\* and 813 cm.<sup>-1</sup> (\* denotes shoulder),  $\tau$  9.12 (singlet, gem-dimethyl) and 9.12 (doublet J = 5.5 c./sec., C<sub>10</sub> methyl) p.p.m. (Found: C, 85.4; H, 14.1. Calc. for  $C_{10}H_{20}$ : C, 85.6; H, 14.4%). The compound showed identical infrared and n.m.r. spectra and g.l.c. chromatograms with 1,1,4-trimethylcycloheptane (VII) prepared from eucarvone.<sup>11</sup>

Hydrogenation of (+)-Car-3-ene at High Pressure. (+)-Car-3-ene,  $[\alpha]_{D}^{20}$  +15.4° (4.3 g.) was hydrogenated in ethanol (30 c.c.) over 5% platinised charcoal at 100 atm. and room temperature. Ether (100 c.c.) was added and the ethanol removed by washing with water (5  $\times$  70 c.c.). Evaporation of the ether yielded carane (98% cis, g.l.c. column (A),  $100^{\circ}$ ) (4.0 g.). Preparative g.l.c. on column (E) at  $120^{\circ}$  gave (-)-cis-carane (VI), which appeared 98.5%pure on g.l.c. column (A) and as a single component on 5 other g.l.c. columns. The pure compound had  $n_{\rm D}^{20}$  1.4548,  $\begin{array}{c} [\alpha]_{\rm p}{}^{20} - 20 \cdot 7^{\circ}, \ \nu_{\rm max}, \ 2992, \ 2917, \ 2867, \ 2717, \ 2617, \ 1468, * \\ 1455, \ 1446, * \ 1419, * \ 1383, * \ 1372, \ 1362, * \ 1341, \ 1305, * \ 1297, \end{array}$ 1284, 1258, 1234, 1222, 1137, 1115, 1079, 1047, 1002, 987, 972, 955, 937, 902, 870,\* 860, 855, 806, 793, 762, 738, and 689 cm.<sup>-1</sup> (\* denotes shoulder),  $\tau$  9.2-9.8 (multiplet, intensity 2, cyclopropane protons), 9.02 (singlet, intensity 3, C<sub>8</sub> methyl), 9.07 (singlet, intensity 3, C<sub>9</sub> methyl), and 9.18 (doublet, intensity 3, J = 5.5 c./sec.,  $C_{10}$  methyl) p.p.m. (Found: C, 87.1; H, 13.3.  $C_{10}H_{18}$  requires C, 86.9; H, 13·1%).

(+)-Car-2-ene.--(+)-Car-3-ene (50 g.) in ethanol (100 c.c.) was stirred at  $20^{\circ}$  under hydrogen at 1 atm. with 5% palladised charcoal (2.0 g.) until 3 litres of hydrogen had been absorbed. G.l.c. of the solution on column (B) at 100° showed the mixture to consist of 1,1,4-trimethylcycloheptane (VII) and *cis*-carane (VI) (22%), car-2-ene (IX) (30%) with a shoulder equivalent to 2.5% 1,1,4-trimethylcyclohept-3-ene (X), and car-3-ene (V) (45%). The mixture (8.0 g.) was chromatographed on a column of silica (0.05-0.2 m.m.) (160 g.) impregnated with 25% silver nitrate. Elution with light petroleum (b. p. 40- $60^{\circ}$ ) afforded (a), 1,1,4-trimethylcycloheptane (VII) and cis-carane (VI), (b), (+)-car-3-ene (V), (c), 1,1,4-trimethylcyclohept-4-ene (XI), and (d), car-2-ene (IX) (2.0 g.) containing about 6% 1,1,4-trimethylcyclohept-3-ene (X).14

Fraction (d) was separated into its components by preparative g.l.c. on column (E) at 120° giving (+)-car-2-ene, paratety equation of the form (L) at 120 groups (F) and 2 only,  $n_{\rm D}^{20}$  1·4753, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +87·6° (c 2·8),  $\lambda_{\rm max.}$  (EtOH) 2110 Å ( $\varepsilon$ 6400),  $\nu_{\rm max.}$  (liq. film) 2899, 2710, 1667 ( $\supset$ C=C $\checkmark$ ) 1445, 1370, 1297, 1211, 1126, 1063, 1020, 1010, 987, 970, 949, 893, 855, 830 (>C=C<H) and 757 cm.<sup>-1</sup>,  $\tau$  9·17 (singlet, intensity 3, C<sub>8</sub> or C<sub>9</sub> methyl), 9—9·3 (multiplet, intensity 2, cyclopropane protons), 8.95 (singlet, intensity 3, C8 or C8 methyl), 8.35 (singlet, broad, intensity 3, allylic methyl), and 4.54 (singlet, intensity 1, olefinic proton) p.p.m. (Found: C, 88.6; H, 11.9. Calc. for  $C_{10}H_{16}$ : C, 88.2; H, 11.8). The minor component consisted of 1,1,4-trimethylcyclohept-3-ene (X), which had identical infrared spectrum and g.l.c. chromatogram (columns B and C) with a specimen prepared as described below.

Fraction (c) after removal of light petroleum, gave a small quantity (estimated as about 4.5% of total products) of 1,1,4-trimethylcyclohept-4-ene (XI), which gave an infrared spectrum and a g.l.c. chromatogram (columns B and C) identical with a specimen obtained as described below.

Disproportionation of (+)-Car-3-ene (V).—(+)-Car-3-ene (40 c.c.) was heated under reflux over 5% palladised charcoal (2.5 g.) for 17 hr. The pale yellow mixture, when analysed by g.l.c. on column (B) at 127° showed four components, the approximate proportions being *p*-cymene (30%), *m*-cymene (20%), 1,1,4-trimethylcyclohept-3-ene (X) (25%), and 1,1,4-trimethylcyclohept-4-ene (XI) (25%). These components were separated by chromatography on preparative column (F) at 105° giving 1,1,4-trimethylcyclohept-3-ene (X),  $n_{\rm p}^{20}$  1.4602,  $v_{\rm max}$ . (liq. film) 1650 ( $\subset$ C=C $\checkmark$ ) 1383, 1362 (gem-dimethyl), and 808 ( $\subset$ C=C $\checkmark$ H) cm.<sup>-1</sup>,  $\tau$  9.08 (singlet, intensity 6, gem-dimethyl) 8:37 (singlet, broad, intensity 3, allylic methyl), and 4.7 (doublet, J =6.5 c./sec., intensity 1, olefinic hydrogen) p.p.m. The compound gave a single peak on g.l.c. on column (B) at 105° (Found: C, 86.8; H, 13.1. Calc. for C<sub>10</sub>H<sub>18</sub>: C, 86.9; H, 13.1%).

Hydrogenation. The cycloheptene (X) (58.2 mg.) was hydrogenated at 1 atm. in ethanol (3 c.c.) over 5% platinised charcoal (32 mg.) and took up 9.0 c.c., corresponding to 0.9 moles, of hydrogen per mole. The product was unresolved from authentic 1,1,4-trimethylcycloheptane (VII) when analysed on column (B) at 104°.

1,1,4-Trimethylcyclohept-4-ene (XI).—This compound, isolated by preparative g.l.c. as for the hydrocarbon (X), had  $n_D^{21}$  1.4536,  $\nu_{max}$ . (liq. film) 1650 ( $\geq C=C \leq$ ) 1375, 1355 (gem-dimethyl), and 856 (-C=C-H) cm.<sup>-1</sup>,  $\tau$  9.14 (singlet, intensity 6, gem-dimethyl), 8.30 (singlet, broad, intensity 3, allylic methyl), and 4.73 (triplet, J = 6 c./sec., intensity 1, olefinic proton) p.p.m. The compound gave a single peak View Article Online on g.l.c. (Found: C, 86.9; H, 13.3. C<sub>10</sub>H<sub>18</sub> requires C, 86.9; H, 13.1%).

Hydrogenation. The cycloheptene (XI) (43.7 mg.) was hydrogenated at l atm. in ethanol (3 c.c.) over 5% platinised charcoal (32 mg.), and took up 7.6 c.c., corresponding to 1.0 moles, of hydrogen per mole. The product was unresolved from authentic 1,1,4-trimethylcycloheptane (VII) on g.l.c. on column (B) at  $104^{\circ}$ .

Equilibration of the Cycloheptenes (X) and (XI).—Each of the cycloheptenes (X) and (XI) (40 mg.) was shaken in ethanol (3 c.c.) at 1 atm. over 5% palladised charcoal (23 mg.) until 1 c.c. of hydrogen had been taken up. G.l.c. analysis of the mixture on column (B) at 127° showed in each case the same mixture of isomers consisting of approximately 64% of (XI) and 36% of (X).

m- and p-Cymenes.—The third fraction isolated by preparative g.l.c. from the disproportionation of car-3-ene was resolved into 2 peaks on column (B) at 100°. The ratio of isomers was 20/30 and the major component was unresolved from authentic *p*-cymene. The mixture had  $\nu_{max.}$  (liq. film) 1605, 1510 (-C=C-), 816, 720 (*p*-cymene, aromatic C-H), 782, and 704 (*m*-cymene, aromatic C-H) cm.<sup>-1</sup> (Found: C, 89.4; H, 10.8. Calc. for C<sub>10</sub>H<sub>14</sub>: C, 89.5; H, 10.5%).

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