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GROUND STATE SIGMATROPIC AND ELECTROCYCLIC REARRANGEMENTS IN SOME MONOTERPENES[1]

THE PYROLYSIS OF α-PINENE

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Abstract—Alloocimene 7, obtained via ocimene 6 by heating α-pinene 2, was further pyrolysed to a complex mixture of products derived primarily from antarafacial 1,7- and suprafacial 1,5-hydrogen migrations, and 6-electron disrotatory electrocyclizations.

Ten years ago we reported[2] that the photochemical isomerization of alloocimene 7 gives two main products. Ground state (thermal) isomerization of the same monoterpene has long been known,[3] and the pyrolysis of its precursor, α-pinene 2, has been extensively studied since 1841.[4] The latter gives two initial products, dipentene 1 (racemic limonene), the pyrolysis of which we describe elsewhere,[5] and *cis*-ocimene 6, which yields only 4-*trans*-6-*cis*-alloocimene 7 (tc).[6] Further pyrolysis gives[7] mainly α-pyronene 8, β-pyronene 9 and the diene 18; minor amounts of the isomers 10, 11, 24, 25, α-terpinene 22 and dipentene 1 were shown indirectly to be present in the pyrolysate, but were not isolated.

This area is now amenable to modern analytical techniques and is of renewed interest since pathways can be rationalized in terms of orbital symmetry: these also lead us to expect[8] the formation of new minor products such as 27 which might be formed concertedly from α-pinene 2 in a chiral suprafacial[1,3] rearrangement with inversion at the migrating carbon. From this work we have concluded[1] that the fastest initial thermal reaction in unhindered 1,3,5-heptatrienes is the [1,7]a-H shift, and we outline here the relative ease of this and the other reactions involved (Scheme 1).

Initially a large-scale pyrolysis of α-pinene 2 was undertaken under conditions whereby the major product, dipentene 1, was largely unaffected so that other pyrolysis products were almost entirely those of alloocimene 7. This permitted identification of many of the minor products, and micro-scale pyrolyses on the glc injection block in conjunction with mass spectrometry (MS) then permitted the further examination of the reaction paths.

RESULTS

Micro-vapour phase pyrolysis of α-pinene 2 on the glc injection block gave results in accord with literature reports when normal packed columns were used. However, with a 100 m capillary column, a more complex pattern emerged. A preparative scale pyrolysis over Pyrex chips at 420° gave a product mixture broadly similar to that obtained by micro-vapour phase pyrolysis at 530° (Table 1) but with larger proportions of aromatic products and small amounts of camphene 4 and tricyclene 5. The crude pyrolysate was separated by distillation and chromatography. Many of the minor components could be isolated, but the main products were characterized by b.ps, spectra, CGMS,[9] dehydrogenation and Diels–Alder reaction with dimethylacetylenedicarboxylate (DMADC) followed by identification of the resulting phthalate. These can readily be distinguished by mass spectrometry since only the C-3- and C-6-substituted isomers can eliminate methanol from the parent ion by a McLafferty rearrangement.[10]

In several cases a diene was synthesized, and relative retention times (RRT) were ascribed to its [1,5]s hydrogen shifted isomers on the basis of the relative areas of new peaks appearing over a range of injection block temperatures.

The most volatile fraction consisted of fragmentation products, all < 1% and not listed in Table 1. Mass spectrometry[9] indicated that isoprene, 2-methylbut-2-ene and toluene were present, probably 2 - methylpent - 2 - ene, and two isomeric methylcyclohexadienes. Glc of the next fraction b.p. 48–54°/20 mm showed a single broad peak, but on the capillary column this was resolved into five main components. α-Pyronene 8 and tricyclene 5 were identified in the earlier distillation cuts of this fraction, while dehydrogenation of later cuts yielded *m*-ethyltoluene (from 24 or 25), 1,2,3 - trimethylbenzene (from α-pyronene 8), 1,2,4 - trimethylbenzene (probably from 13 or 14 or their 1,5 - hydrogen shifted isomers) and 1,2,3,5-tetramethylbenzene (from 12). The presence of the homoannular dienes 24 and 25 was confirmed by injection block pyrolysis of a mixture of the *trans* isomers of trienes 19 and 23: these trienes were obtained, together with the alloocimenes 7(tt) and 7(tc), on dehydration of a mixture of the corresponding dienols. The diene 24, the initial cyclization product, is isomerized to 25 as the temperature is raised; it was also observed[5] as a pyrolysis product of limonene 1. The dienes 17 and 18 are also major products of the pyrolysis of 19 and 23.

The next pyrolysis fraction b.p. 54–60°/20 mm consisted mainly of a mixture of the dienes 17 and 18. The formation of the diene 18 was reported by Parker and Goldblatt[9] on pyrolysis of alloocimene (7tt and 7tc) but

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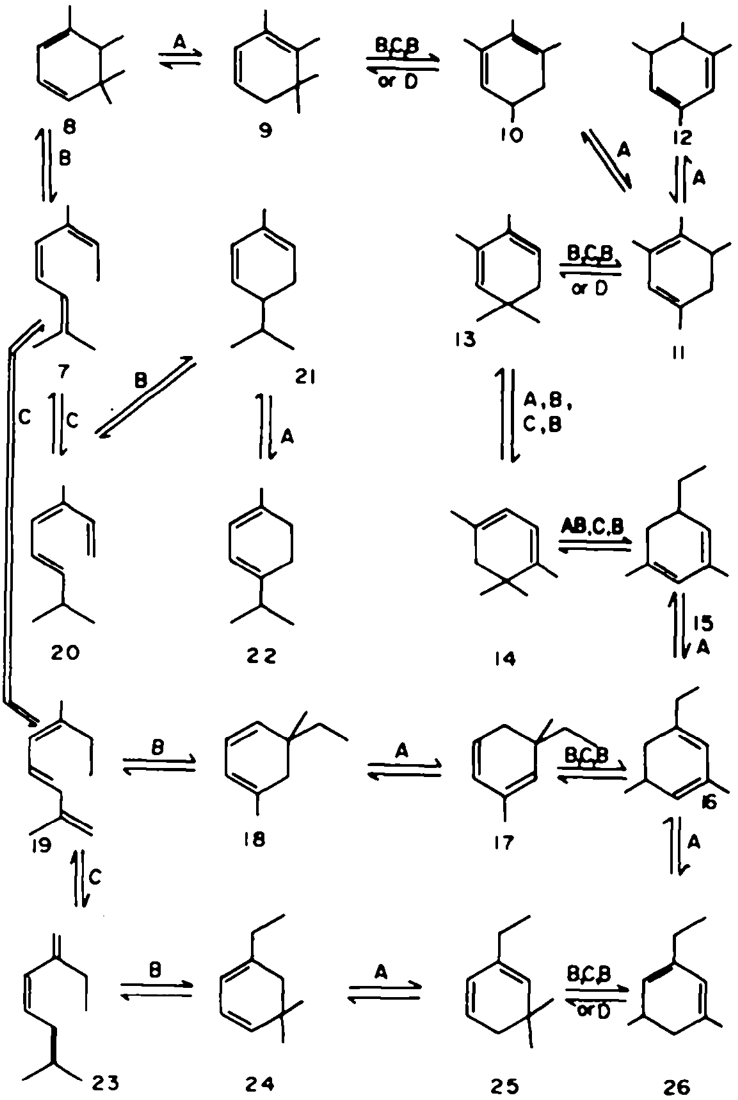

Scheme 1.

A = [1,5]s H shift; B = [3,3] electrocyclic ring opening or closing; C = [1,7]A H shift; D = [1,5]s CH_3 shift.

their sample very probably also contained the diene 17. The two dienes were inseparable by glc but the increase with b.p., in the low-field (τ 4.1–4.5) portion of the complex olefinic NMR signal is consistent with an increasing proportion of 17. This was confirmed by Diels–Alder condensations with DMADC, which resulted in a higher ratio of methyl 4-methylphthalate to the 3-Me isomer from higher boiling fractions of the diene (17 and 18) mixture. A minor constituent of this fraction, the vinylcyclohexene 3, was identified by glc and its very characteristic mass spectrum: it arises, apparently, by minor pyrolytic decomposition of the major pyrolysis product, dipentene 1.[5] Camphene 4 and tricyclene 5 were separated from the conjugated diene isomers of similar volatility by treatment with maleic anhydride, and were identified by GCMS and IR. Neither 4 nor 5 was observed on pyrolysis on the glc injection block, and their formation over Pyrex chips is analogous to their synthesis[4d] from α-pinene 2 over hot mineral clays.

The higher-boiling fractions contained β-pyronene 9 and dipentene 1, isolated by distillation, and α-phellandrene 21, α-terpinene 22, p-cymene and two alloocimenes 7 (tc and tt), identified by GCMS. Dehydrogenation of the fraction b.p. 63–68°/20 mm yielded p-cymene, 1,2,4- and 1,2,3 - trimethylbenzenes, 1,2,3,5 - tetramethylbenzene and 1,3 - dimethyl - 5 - ethylbenzene. The latter arises from 15, 16 and 26, and the tetramethylbenzene from 10 and 11. The genesis of the other benzenes is evident apart from 1,2,4 - trimethyl-, which could be formed from 13 and 14 or their 1,5-hydrogen-shifted isomers, but no other evidence for the presence of these compounds could be obtained.

The diene 15, synthesized from 5 - ethyl - 3 - methylcyclohexenone as described,[11] was pyrolysed by glc, and yielded first one isomer (16), then a second (26), of shorter retention time, as the injection block temperature was raised (Table 2). Grignard reaction of 3,5,6 - trimethylcyclohex - 2 - enone[12] with methyl iodide resulted in spontaneous dehydration to a mixture of dienes, 11 and 12. These were separated by glc and distinguished spectroscopically. Pyrolysis of 11 gave 12, while the latter gave 10 and 11 as a single broad glc peak (Table 2). In the α-pinene 2 pyrolysate, peaks corresponding to these dienes were observed.

Table 1. Micro vapour phase pyrolysis on the glc injection block

<table>
<tr><th>Compound</th><th>8</th><th>25</th><th>12</th><th>24</th><th>2</th><th>17</th><th>18</th><th>3</th><th>9</th><th>26</th><th>e</th><th>16</th><th>10</th><th>11</th><th>15</th><th>21</th><th>22</th><th>1</th><th>6</th><th>7ct</th><th>7tc</th><th>7tt</th></tr>
<tr><th>Temp.^{b} RRT^a</th><th>1.29</th><th>1.32</th><th>1.37</th><th>1.41</th><th>1.41</th><th>1.61</th><th>1.61</th><th>1.68</th><th>1.93</th><th>1.93</th><th>1.96</th><th>2.07</th><th>2.07</th><th>2.07</th><th>2.2</th><th>2.28</th><th>2.37</th><th>2.61</th><th>2.61</th><th>3.5</th><th>4.95</th><th>5.35</th></tr>
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<tr><td>600</td><td></td><td></td><td></td><td colspan="2"></td><td colspan="2">3</td><td>4</td><td colspan="2">4</td><td>2</td><td colspan="3">5</td><td>2</td><td></td><td>1</td><td colspan="2">9</td><td></td><td></td><td></td></tr>
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<tr><td>(c)</td><td>+</td><td>+</td><td>+</td><td>+</td><td></td><td></td><td></td><td></td><td>+</td><td>+</td><td>+</td><td>+</td><td>+</td><td>+</td><td>+</td><td></td><td>+</td><td></td><td></td><td></td><td></td><td></td></tr>
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</table>

\+ corresponds to identification by the indicated method

a relative retention time (RRT) to m-xylene (1.00) on a 100 m capillary column containing squalane at 70°: only peaks >0.75% of the total area are included. m-Xylene (RRT 1.00), m-ethyltoluene (1.65) and p-cymene were formed at 530°, and 1,3-dimethyl-5-ethylbenzene (3.25), 1,2,4-(2.07) and 1,2,3-trimethylbenzene (2.57) and 1,2,3,5-tetramethylbenzene (5.1) appeared at higher temperatures. Camphene (4) (RRT 1.75) and tricyclene (5) (1.51) were present and identified only in the large scale pyrolysis, neither *cis*-ocimene (6) nor its *trans*-isomer were detected and the two 4-*cis*-allocimenes were tentatively identified in the hot-wire pyrolysis of α-pinene.

b injection block temperature: residence *ca*. 0.5 sec.

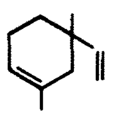
c indicates dehydrogenation to the corresponding substituted benzene.

d indicates identification of the appropriate dimethylacetylenedicarboxylate (DMADC) adduct.

e p-mentha-2,8-diene: the large scale pyrolysis of α-pinene yielded a small amount of p-mentha-2,8-dien-1-ol, possibly by autoxidation of this hydrocarbon.

Table 2. Micro vapour phase pyrolysis of synthetic dienes

Temp.	GLC Analysis		
	15	16	26
150	99		
400	70	16	2
425	43	30	18
435	35	31	25
450	31	29	27
	10 + 11	12	
150	92		
430	76	6	
490	65	26	
150		98	
430	49	46	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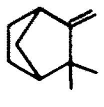
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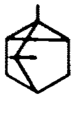
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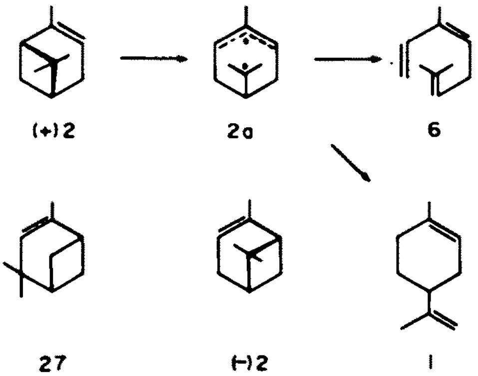


Scheme 2.

The remaining products were identified as shown in Table 1.

DISCUSSION

Burwell[13] has suggested that the common intermediate in both the formation of dipentene 1 and *cis*-ocimene 6 and the racemization of α-pinene 2 is the biradical 2a (Scheme 2). An alternative multicentred transition state has been proposed[14] but is unsatisfactory on orbital symmetry grounds: the more acceptable variant involving a homodienyl 1,5-hydrogen migration would give rise to optically active limonene, known[5] to be stable under the pyrolysis conditions. Furthermore the racemization of α-pinene, which occurs at about the same rate as dipentene formation, is not explained by this mechanism. A retro-Diels–Alder ($-[\pi 4s+\pi 2s]$) reaction to give 6 from 2 is also conceivable, but it is energetically unfavoured, and no other products attributable to this mechanism have been observed.

Another isomerization, firmly established for some bicyclo [3,2,0] heptenes[8b] and potulated[8a] for the α-pinene ring system, is a [1,3]s rearrangement involving rebonding of the back lobe of the breaking cyclobutane sigma bond. This might be expected to give rise to 27, reduced steric hindrance in the product being a feasible driving force, but no trace of such a product was detected. The alternative [1,3]s migration to give inversion of (+)-2 to (−)-2 would involve a twisting of the gem-dimethyl group through the plane of the ring, and can thus be discounted.

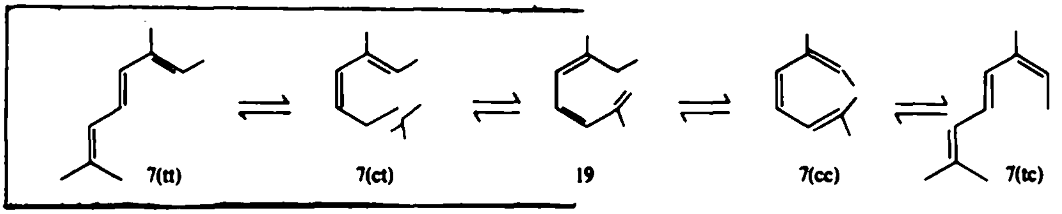
On the basis of calculations[15] for the opening of cyclobutane to two ethylene molecules one could envisage a smooth one-step process for the isomerization of α-pinene 2 to ocimene 6, passing through the biradical species without the latter becoming a discrete intermediate. But to explain the racemization on formation of dipentene the biradical 2a must have a finite existence, in accord with the postulate of Burwell.[13] 4 - *trans* - 6 - *cis* - Alloocimene 7 (tc), the sole initial product[6] of heating *cis*-ocimene 6, cannot itself cyclize to a cyclohexadiene, but must first yield a 4-*cis*-alloocimene. Under most pyrolysis conditions only the two 4-*trans* isomers are observed, but we have detected the formation of the two 4-*cis* isomers 7(cc) and 7(tc) and *cis*-ocimene 6 in low yield on pyrolysis of α-pinene 2 over a hot wire.[5] α-Pyronene 8 must arise in a disrotatory electrocyclization from 7(ct) or 7(cc). β-Pyronene 9 is formed from 8 by a normal [1,5]s hydrogen shift while the other major pyrolysis product, the diene 18, is formed from 7(ct) or 7(cc) via a [1,7]a hydrogen shift, followed by electrocyclization of the resulting triene 19. In fact all the reactions shown in Scheme 1 can be explained on the basis of a series of [1,5]s and [1,7]a hydrogen shifts, electrocyclizations and reversions, as illustrated. We believe that the formation of the diene 10 from β-pyronene 9 occurs via the two corresponding open chain trienes, interconverting by a [1,7]a hydrogen shift, but we have not been able rigidly to exclude the possibility of the direct isomerization 9→10 by a [1,5]s Me shift, for which analogies have been reported.[16] Similarly the direct isomerizations 18→24, 17→16, 11→13 and 25→26 can be envisaged, but in view of the facility of the isomerization of α-pyronene 8 to 18 (Table 3) which *must* proceed through the open chain trienes, the contribution of [1,5]s methyl shifts in these series is surely, at most, minor.

Evidence for these pathways, and of the relative ease of the steps involved, comes from the results given in Tables 1 and 3. Significant (>5%) interconversion of the two 4-*cis*-alloocimenes 7(cc) and 7(ct) occurs at 200° and cyclization of these takes place at 300°; *cis* to *trans* isomerization about the central double bond to yield 4-*trans*-alloocimenes 7(tc) and 7(tt) occurs (>5%) at 360° and the reverse (terminating in α-pyronene 8) at 412°. Isomerization about the terminal double bond of 4-*trans*-alloocimenes becomes apparent only at about 450°, while reformation of trienes from pyronenes 8 and 9 becomes significant only at 500°. Analogous steps at very similar temperatures are evident on pyrolysis of α-phellandrene 21 and its related trienes under these conditions.[1]

The first reaction, interconversion of 7(cc) and 7(ct) could, in principle, occur by (i) reversible ring closure to the cyclohexadiene or (ii) direct rotation about the terminal double bond, or (iii) two consecutive 1,7-hydrogen shifts via **19**. We can disregard both (i), since α-pyronene **8** is neither formed nor opened at these temperatures, and (ii), since interconversion of the two 4-*trans*-trienes, which would also occur by this mechanism, takes place only at much higher temperatures. The mechanism (iii) is further supported by the similar pyrolysis of the trienes derived from α-phellandrene **21**. These appear to be the first clear instances of [1,7]a-H migration in open chain trienes.[16]

There are two possible precursors in the second reaction, cyclization, and in neither the α-pyronene **8** nor the α-phellandrene **21** formation can we distinguish between them. In an analogous disrotatory cyclization, Marvell[17] found that only *trans* - 5,6 - dimethylcyclohexadiene is formed from a mixture of *cis, cis, cis*- and *cis, cis, trans*-octa-2,4,6-trienes. This suggests that the less hindered triene, 7(ct) in the present case, undergoes cyclization more readily. Conversely the more hindered triene is *formed* on conrotatory photochemical ring opening of both α-pyronene **8**[2] and α-phellandrene **21**[18] but this appears to be a function of the ground-state conformation of the diene.[19]

The next reaction, [1,5]-hydrogen chift, is unexceptionable, and the isomerization about the central triene double bond through a bi-allylic biradical has many precedents.[20] However, the pathway of isomerization about the terminal double bond for 7tc⇌7tt is unclear: it could be direct, with conjugative stabilization of only one side of the intermediate orthogonal biradical, or multistep, by the lower energy pathway:



The main thermal reactions encountered in this work are summarized, in order of decreasing facility, in Table 4.

The electrocyclization processes described here were also observed to have their parallel among the odd electron molecular ions generated in mass spectrometry. Such open shell species in high vibrational states

Table 3. Micro vapour phase pyrolysis of α- and β-pyronene, and alloocimene

Block temp.	8	17,18	9	10,11,16	7 cc	6[a]	7 ct	7 tc	7 tt
70									99
375	4	1	1		1		1	1	90
412	10	4	10		1		1	3	65
450	20	16	28		3		1	5	21
70	99								
350	75		25						
450	39		61						
500	17	11	26	7	3			3	4
70			99						
350	11		89						
415	39		60						
450	33		47						
500	19	11	27	7	4			3	5
70					100				
170					96			2	2
230					80		15	3	2
313	6				49		40	2	1
360	30	6	3		31		20	5	5
400	35	11	18		14		5	8	9
70						88	5		
350	4				4	21	6	58	
375	10	2	2			15	3	52	7

[a] This sample of ocimene contained 12% limonene 1 which is not affected under the conditions used: general conditions as in Table 1.

Table 4. Summary of thermal reactions

Reaction	Temp.(°C) of occurrence (>5%)	E_a for analogous reactions (Kcal/mol)
[1,7]-H shift	200[a,b]	15-21[16]
[3,3] closure	300[a] 280[b]	29-33[21]
[1,5]-H shift	330[a] 350[b]	32-35[16]
central C=C isomerization	360[a] (ct→tt) 380[a] (tt→ct)	42.4 [22]
terminal C=C isomerization	440[a]	45.0[c.]
[3,3] opening	500[a]	52.8[24]

a alloocimene series

b α-phellandrene series

c for 2,3-dimethylpenta-1,<u>cis</u>-3-diene, <u>via</u> the corresponding cyclobutene 23

undergo ring closure to the corresponding cyclohexadiene species with very little detectable [1,7]-hydrogen migration. Thus the mass spectra of the pyronenes 8 and 9 are almost identical[25] with those of all four of the alloocimenes 7: those of the isomeric trienes 19(tc) and 19(tt) (the two isomers *cis* at the central double bond were not isolated) and the dienes 17 and 18 are indistinguishable. Likewise the triene 23(t) exhibits a spectrum almost identical with that of 24 but distinct from those of 19 and 7. The main fragmentation pathway which would be expected from trienes would normally be simple allylic cleavage. However, consideration of the heats of formation of fragment ions clearly indicates a preference for alkyl substituent loss (Et > Me > H) which is achieved most easily by direct cyclization of the triene. A comparison of the spectra of 3,4,5,6 - tetra - methyl - octa - 2,4,6 - triene(cct)[26] and its ring-closed isomer 1,2,3,4,5,6 - hexamethylcyclohexa - 1,3 - diene indicated that this cyclization phenomenon was not confined to terpene triene molecular ions.

EXPERIMENTAL

Unless otherwise stated UV spectra were recorded in EtOH. IR spectra as neat liquid films and NMR at 60 MHz in CCl_4. Glc injection block pyrolyses were carried out on a Perkin Elmer F-11 instrument, which is particularly suited to this application: samples of 0.2 μl were injected, the syringe needle being allowed to protrude 2 cm past the septum, in a glass injection port liner. The pyrolysis products were separated on a 100 m × 0.02 in squalane capillary column at 90° and 30 psi N_2 pressure Mass spectra (MS) were recorded at 70 eV with an ion source temp. of 150° on a Perkin Elmer RMS-4 single focussing instrument. All GCMS spectra were obtained using He as carrier gas and Carbowax 20 M (2 m × 1/8 in) for separations. Distillations were carried out on a 36 in spinning band column and on a high speed adiabatic spinning annulus column (Nester-Faust NFT 51). Dimethylacetylenedicarboxylate (DMADC) adducts were obtained by refluxing equal amounts of ester and hydrocarbon without solvent for 5 hr.

α-Pinene pyrolysis. The pyrolysis "oven" was a vertically mounted (0.6 m × 40 mm i.d.) Pyrex tube, heated electrically by an externally wound nichrome wire and insulated with asbestos rope and aluminium foil. An inner tube (0.7 m × 30 mm i.d.) containing Pyrex chips and a Pyrex-sheathed thermocouple, was surmounted by a pressure-equalizing funnel. α-Pinene (1342 g) was passed, during 9.5 hr, through the apparatus at 420°, with a N_2 flow of 30–40 ml/min. The pyrolysate was condensed into an ice-cooled flask and separated on a large spinning band column into four distillate fractions, which were carefully redistilled.

The most volatile components, b.p. up to 47°/20 mm (40 g), were examined by GCMS, and isoprene, toluene and 2 - methyl-but - 2 - ene were positively identified. The remaining volatile components appeared, from their mass spectra[9] to be 2-methyl-pent-2-ene and two isomeric methylcyclohexadienes.

The fraction b.p. 48–54°/20 mm (142 g) yielded 8, b.p. 48°/20 mm (IR, NMR, GCMS) and a mixture containing (capillary glc) the isomers 2, 12, 24 and 25. Authentic samples of 24 and 25 were synthesized on the glc injection block by cyclization of the triene 23 (see below). When refluxed overnight with 10% Pd/C this fraction yielded (GCMS) *m*-ethyltoluene, 1,2,4-trimethylbenzene, 1,2,3 - trimethylbenzene and 1,2,3,5 - tetramethylbenzene which were compared with authentic samples.

A mixture of a pyrolysate fraction b.p. 47–56°/20 mm (3.3 g) and maleic anhydride (3.3 g) was slowly (30 min) heated to 140°, cooled, basified and steam distilled. The resulting oil (550 mg) contained mainly 4 (25%) and 5 (37%), which were both separated by glc and identified by IR. The fraction b.p. 54–60°/20 mm (215 g) consisted mainly of an inseparable mixture of 18 with increasing amounts (determined by NMR) of the isomer 17 as the distillate temp. rose. It showed strong IR absorption at 725 cm^{-1} and *m/e* (invariant with changing ratios of 17/18) 136 (21) 121 (15), 108 (10) 107 (100), 93 (30) 91 (44), 79 (13), 77 (13), 69 (5), 67 (6), 65 (8), 55 (6), 53 (8) and 51 (5%), and complex olefinic NMR signals. With DMADC a fraction b.p. 57–8°/20 mm gave (glc–OV-17 column) two phthalate esters, RRT 1.0 (61%) and RRT 1.2 (39%), while a fraction b.p. 58–9°/20 mm gave the same phthalates in the proportions 54% and 46% respectively: elution from silica with light petroleum–ether gave first methyl 3-methylphthalate (RRT 1.0) then the 4-methyl phthalate (RRT 1.2) identical (IR, NMR, MS) with authentic samples.[27] The 3-Me isomer was also obtained from α-pyronene by this method.

The non-conjugated diene, 3,[5] was detected on the squalane capillary column in some fractions of the mixture of dienes 17 and 18, and was identified by its large *m/e* 68 signal.

The remaining pyrolysis products were identified by the methods indicated in Table 1. β-Pyronene b.p. 61–63°/20 mm (104 g) was isolated by distillation, and a part of the fraction b.p. 63–68°/20 mm (46 g), refluxed overnight with 10% Pd/C, yielded (GCMS) mass spectra and RRT identical with those of authentic *p*-cymene, 1,2,3 - trimethylbenzene, 1,2,4 - trimethylbenzene, 1,3 - dimethyl - 5 - ethylbenzene and 1,2,3,5 - tetramethylbenzene.

Preparation of the trienes 19*tc*, 19*tt* *and* 23*t*. A mixture* (20 g) of 6 - hydroxy - 2, 6 - dimethylocta - 2, 4 - diene and 2 - hydroxy - 2,6 - dimethylocta - 3,5 - diene was stirred at 50° with conc. HCl (5 ml). After 30 min the product, containing 19tc (19), 23t (18), 19tt (16), 7tc (21) and 7tt (25%) (longer times resulted in the formation of more 7) was isolated and distilled into two fractions. The first contained 19 (tt and tc) and 23t, identified by their (GCMS) mass spectra, which were virtually identical with those of their cyclized isomers, 18 and 24 respectively. This mixture (23t, 28%; 19tc, 24%; 19tt, 43%) yielded 8 (3%), 24 (9%), 25 (3%), 17 and 18 (10%), 7tc (2%), 7tt (2%) as well as unchanged starting material when pyrolysed on the glc injection block at 450°.

Synthesis of the dienes 11 and 12. Mg turnings (7.3 g) were covered with anhyd ether (50 ml) and, under N_2, MeI (42.6 g) in ether (150 ml) was added, followed by a crystal of I_2. When reaction had subsided 3,5,6 - trimethycyclohex - 2 - enone[12] (20 g) in ether (100 ml) was added during 2 hr and the mixture maintained at reflux for 3 hr. Saturated NH_4Claq. (200 ml) was added, and the ppt washed with ether (3 × 100 ml). The combined dried ($MgSO_4$) ether solns yielded a mixture of 11 and 12 (4:1) (15.6 g) which was distilled and separated by preparative glc. 1,3,4,5 - *Tetramethylcyclohexa* - 1,3 - *diene* 11 (92%) had ν_{max} 2980 (S), 2910 (S), 1665, 1648, 1608, 1452 (S), 1421, 1375 (S), 1363, 1308, 1242, 1221, 1195, 1015, 880, 848 and 816 cm^{-1}, τ ($CDCl_3$) 4.51 (1H, s), 7.5–8.5 (3H, m), 8.36 (9H, br s) and 9.04 (3H, d, J 6Hz), *m/e* 136 (M^+, 30), 121 ($M^+ - 15$, 100), 107 (7), 106 (9), 105 (53), 91 (24), 79 (24), 77 (20), 67 (8) and 65 (6%) (Found: C, 88.1; H, 11.6. Calc. for $C_{10}H_{16}$: C, 88.2; H, 11.8%). 1,3,5,6 - *Tetramethylcyclohexa* - 1,3 - *diene* 12 (98%) had ν_{max} 2800, 2620, 2370, 1665, 1598, 1450 (S), 1375 (S), 1365, 1352, 1278, 1207, 1158, 1102, 1035, 1020, 1000, 992, 974, 847 and 805 (S) cm^{-1}, τ 4.59 (1H, s), 4.82 (1H, br s), 7.7–8.5 (2H, m), 8.27 (3H, s), 8.33 (3H, s), 9.09 (3H, d, J 7Hz) and 9.15 (3H, d, J 7Hz), *m/e* as for 11.

Synthesis of 1,3 - *dimethyl* - 5 - *ethylcyclohexa* - 1,3 - *diene* 15. 5 - Ethyl - 3 - methylcyclohex - 2 - ene - 1 - one, prepared as described[29] had λ_{max} 240 nm (ϵ = 4600), ν_{max} 1670 (S), 1630, 1462, 1452, 1410, 1382, 1300, 1264, 1250, 1167, 1147, 924, 890 (S), 830, 810 and 778 cm^{-1}, τ 4.3 (1H, s), 7.5–8.3 (5H, m), 8.07 (3H, s), 8.65 (2H, q, J 6Hz) and 9.06 (3H, t, J 6Hz), *m/e* 138 (M^+, 22), 110 (3), 109 (2), 83 (10), 82 (100), 81 (7), 55 (7), 54 (10), 53 (9), 41 (11) and 39 (20%). The ketone, treated with MeMgI as described above, afforded a mixture of equal parts of the reported[11] dienes b.p. 68–70°/20 mm. Preparative glc yielded the endocyclic diene 15, λ_{max} 267 nm (ϵ = 2300), ν_{max} 1656, 1450 (S), 1374 (S), 1204, 1147, 1060, 1034, 1016, 960, 856, 840, 832, 817 and 788 (S) cm^{-1}, τ 4.55 (1H, s), 4.8 (1H, s), 7.6–8.1 (3H, m), 8.23 (3H, s), 8.35 (3H, s), 8.72 (2H, q) and 9.12 (3H, t), *m/e* 136 (M^+, 33), 121 (9), 107 (100), 105 (18), 93 (8), 91 (40), 79 (12), 77 (9), 67 (5), 55 (8), 53 (7), 51 (6) and 43 (10%). (Found: C, 87.9; H, 12.0. Calc. for $C_{10}H_{16}$: C, 88.2; H, 11.8%) and 5 - ethyl - 1 - methyl - 3 - methylenecyclohex - 1 - ene, λ_{max} 1648 (S), 1610 1224, 1150, 1105, 1020, 890 (S), 866 (S), 840 and 770 cm^{-1}, τ 4.12 (1H, br s, HC=), 5.29 (2H, br s, H_2C=), 7.5–8.85 (10H, m) and 8.9–9.3 (3H, m), *m/e* 136 (M^+, 48), 121 (23), 107 (100), 105 (13), 93 (39), 91 (50), 79 (50), 77 (17), 65 (10) and 40 (13%).

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