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STUDIES IN THE PINANE SERIES

THE SYNTHESIS OF (±) "ORTHODENE"[1]

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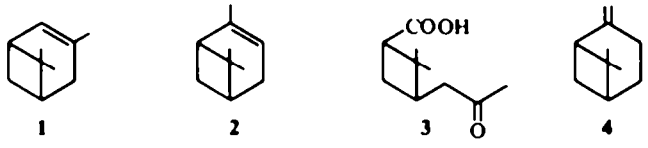
Abstract—The conversion of 6,6-dimethylbicyclo[3.1.1]heptan-3-one into 3,6,6-trimethylbicyclo[3.1.1]-heptene-2 ("orthodene"), formerly considered to be a naturally occurring isomer of α-pinene, is described.

THE bicyclic hydrocarbon "orthodene" (**1**), a little known isomer of α-pinene (**2**), was first reported by Fujita in 1933[2] as a constituent of the essential oil of *Orthodon lanceolatum*, Kudo (*Labiatae*). Subsequently, the same author recorded the occurrence of the compound in the leaf oil of camphor seedlings and in mature plants of the genus *Orthodon*.[3] As evidence for structure **1**, Fujita described[2] an oxidation product which he formulated as **3**. Later, Guha and Rao[4] synthesized racemic (supposedly *trans*) **3** and found that it had different properties.



1 **2** **3** **4**

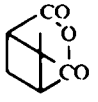
In this paper we describe a number of synthetic routes to the racemic form of **1**, the b. p, refractive index, and density of which were found to differ from those recorded for "orthodene". After completion of our work we learned that Klein and Rojahn[5]* have recently synthesized **1** by a pathway similar to one employed by us. These authors note that the m. p. of **3** as obtained by permanganate oxidation of racemic **1** differs significantly from that of the acid described by Fujita. They also report that according to Professor S. Saito of Meiji University, Tokyo, "orthodene" has now been identified as β-pinene (**4**).**

In our approaches to **1**, a route involving the bicyclic ketone **7**, isonopinone, proved to be the most satisfactory. Originally, we set out to prepare **7** from *cis-syn*-homopinic acid (**6d**). The latter was synthesized in pure form from norpinic anhydride (**5**) via the diol **6a**, and thence the bismethanesulfonate **6b**, and the dinitrile

* We thank Dr. Klein for kindly informing us of his work prior to publication.

** We are indebted to Professor Saito for further correspondence on this matter. According to Fujita,[2] α-pinene (**2**) was also present in the "orthodene" fraction.

6c. Alternatively, a 70:30 mixture of *cis*- and *trans-sym*-homopinic acid[6] was obtained from the monoethyl ester **8a**[7,*] of a similar mixture of racemic *cis*- and *trans*-pinic acid by Arndt-Eistert homologation and from racemic *cis*-pinonic acid (**8b**)[8] by the Kindler modification of the Willgerodt reaction.[6] Unfortunately, Dieckmann cyclization of the dimethyl ester of *cis*-**6d** could be made to yield **7** in only trace amounts. By contrast, the related Dieckmann cyclizations leading to pinocamphone (**9**) and thujone (**10**) have been reported to proceed in about 20% yield.[9]



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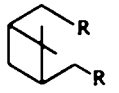
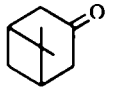


6a: R = OH
b: R = $MeSO_3$
c: R = CN
d: R = COOH



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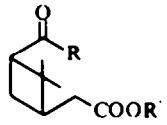
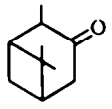


8a: R = OH; R' = Et
b: R = Me; R' = H



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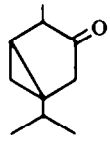

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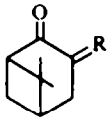
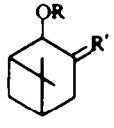
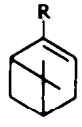
In view of these unsatisfactory results, an alternative route to **7** was sought from nopinone (**11a**), an ozonization product of β-pinene (**4**). The benzylidene derivative **11b**[10] was reduced with LAH to the corresponding allylic alcohol **12a**, which on ozonolysis of the acetate gave the solid α-acetoxyketone **12b**, mp 95·5–96·5°. However, even under the best conditions that could be found, **12b** was obtained in only 7% yield. Deacetoxylation of **12b** could not be effected by reaction with zinc in hot acetic anhydride but was achieved with calcium in liquid ammonia.[11] Oxidation of the crude product then afforded isonopinone (**7**) in reasonably pure form. The overall yield of isonopinone from nopinone, however, was far from satisfactory.



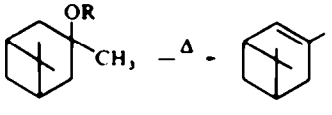
11a: R = H_2
b: R = CHØ
c: R = CHOH



12a: R = H; R' = CHØ
b: R = Ac; R' = O



13a: R = CHO
b: R = H



14a: R = H
b R = 3,5-DNB

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15

16a: R = H
b: R = 3,5-DNB

* We thank Dr. Hedrick for generous gifts of compounds **8a** and **8b**.

Fortunately, during the course of these studies a new, more direct route to isonopinone became available. The oxidation of α-pinene (**2**) to myrtenal (**13a**) by selenium dioxide proceeds in fair yield,[12] and decarbonylation of the aldehyde to apopinene (**13b**) over Pd–$BaSO_4$ has been described.[13] Hydroboration of apopinene, followed by oxidation of the resulting alcohols, has been reported[14] to yield mainly isonopinone (**7**) plus some nopinone (**11a**). In our hands this procedure afforded a 68% yield of a 7:1 mixture of **7** and **11a** from apopinene. Fractional distillation gave **7** in better than 98% purity. Very recently the preparation of **7** in 40% yield from apopinene oxide by base-catalyzed rearrangement with lithium ethylamide has been described.[15]

Although isonopinone has a strong tendency to enolize in the presence of methylmagnesium iodide (but apparently not in the presence of $MeMgBr$[5]), it reacted smoothly with methyllithium at low temperature to give the expected alcohol, **14a**, which was readily purified through the 3,5-dinitrobenzoate (**14b**), obtained in 38% yield from **7** after crystallization to constant melting point of 137° (dec). In order to verify that this derivative was formed from the ketone **7** and not from nopinone (**11a**), the 3,5-dinitrobenzoate (**16d**) of alcohol **16a*** was prepared from nopinone and found to melt at 84° (dec). Gas chromatographic analysis of the volatile material produced during the melting of **16b** showed that 34% of α-pinene (**2**) and 43% of β-pinene (**4**) were formed. At 140° α-pinene was obtained in 10% yield, and no β-pinene could be detected. Apparently products of rearrangement predominated at the higher decomposition temperature.

When heated at 140–180° under reduced pressure,[16] **14b** furnished an equimolar mixture of **1** and the exocyclic isomer **15** in quantitative yield. The two olefins were isolated in pure state by preparative gas chromatography. Spectral data and the direct synthesis of **15** from **7** by the Wittig reaction confirmed the structural assignments. Treatment of **15** with N-lithioethylenediamine[17] gave **1** in 92% yield under conditions that convert β-pinene quantitatively into α-pinene. As already noted, the b.p., refractive index, and density of **1** as prepared by synthesis do not agree with the corresponding data recorded[2] for "orthodene".

Before concluding, one other approach to **1** deserves brief mention. Catalytic hydrogenation of the hydroxymethylene derivative **11c** of nopinone (**11a**) to yield 2-methylnopinone (**17**) has been described.[18] Reduction of **17** with LAH furnished a

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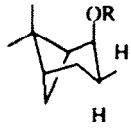
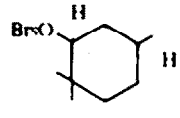


18a: R = H
b: R = *p*-BrØSO_2



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liquid alcohol whose probable configuration (**18a**) renders it unsuitable for dehydration via ester pyrolysis. Attempted dehydration by base-catalyzed elimination of the *p*-bromobenzenesulfonate ester **18b** did not prove feasible, since rearrangement to the brosylate **19** appeared to be favored in the preparation of **18b**.[19] In view of this sensitivity of the bicyclo[3.1.1]heptan-2-ol system to rearrangement under

* For evidence on stereochemistry, see D. V. Banthorpe and D. Whittaker, *Chem. Revs.* **66**, 643 (1966).

acidic conditions, our inability to obtain **1** from **18a** by dehydration is not surprising. A further attempt to prepare **1** via reduction of the isopropyl ether of **11c**, followed by hydrolysis to the Δ^2-3-formyl derivative and then Wolff-Kishner reduction, was also unsuccessful.

EXPERIMENTAL

M.ps were determined in capillary tubes and are corrected; b.ps are uncorrected. UV spectra were measured in 95% EtOH. NMR spectra were recorded on a Varian A-60 instrument with TMS as internal standard. Petroleum ether refers to the fraction with b.p. 35–45°.

1,3-cis-*Bis(hydroxymethyl)*-2,2-*dimethylcyclobutane* (**6a**)

A soln of 7·7 g (0·05 mole) of **5**[10] in 125 ml anhyd ether was added dropwise to a stirred slurry of 1·9 g (0·05 mole) LAH in 200 ml ether under dry N_2. After 9 hr, an additional 1·9 g LAH was added and the mixture allowed to stir overnight. After cautious addition of sat Na_2SO_4aq (10 ml) and then anhyd Na_2SO_4 (25 g), the mixture was filtered and the filtrate concentrated to a damp solid. This was dissolved in CH_2Cl_2 and the water removed by azeotropic distillation. Evaporation of the solvent gave 4·4 g (65%) of small white plates which on sublimation (45°, 0·07 mm) afforded pure diol **6a**, m.p. 60–61·5°; IR ($CHCl_3$) absorption at 2·37 and 2·87 μ; NMR (CH_2Cl_2) signals at 6·40 (4H, d, J = 7 c/s), 8·80 and 8·95 τ (6H, s). (Found: C, 66·82; H, 11·22. $C_8H_{16}O_2$ requires: C, 66·63; H, 11·18%.)

1,3-cis-*Bis(hydroxymethyl)*-2,2-*dimethylcyclobutane dimethanesulfonate* (**6b**)

To an ice-cold soln of 1·44 g (0·01 mole) crude diol **6a** in 10 ml CH_2Cl_2 and 2 ml dry pyridine was added, with swirling, 2·5 g (0·022 mole) methanesulfonyl chloride. After chilling at 0° for 6 hr, the mixture was allowed to stand at room temp overnight. It was then washed with two 10-ml portions of cold water and the organic layer dried (Na_2SO_4). An oil, which crystallized readily on seeding, was isolated on evaporation of the solvent. The crude product, when washed with pet. ether, collected, and dried, amounted to 2·96 g (99%). Pure dimesylate **6b** crystallized from a mixture of EtOAc–pet. ether as small, white prisms, m.p. 75–76°; IR ($CHCl_3$) absorption at 7·40, 7·50 and 8·52 μ; NMR (CH_2Cl_2) signals at 5·82 (4H, d, $J \sim 7$ c/s), 7·01 (6H, s), 8·79 and 8·90 τ (6H, s). (Found: C, 39·98; H, 6·86; S, 21·40. $C_{10}H_{20}O_6S_2$ requires: C, 39·98; H, 6·71; S, 21·35%.)

cis-sym-*Homopinic acid* (**6d**)

A mixture containing 3·0 g (0·01 mole) of **6b**, 4·0 g (0·08 mole) of dry, reagent-grade NaCN and 85 ml anhyd DMSO was stirred, under dry N_2, for 72 hr at 40°. The reaction mixture was diluted with 150 ml sat NaClaq. Just enough water was then added to dissolve the pptd salts, and the mixture was extracted with four 50-ml portions of CH_2Cl_2. The combined organic layers were washed with two 50-ml portions of sat NaClaq and dried (Na_2SO_4). Removal of the solvent gave crude dinitrile **6c**; IR ($CHCl_3$) absorption at 4·46 μ.

A soln of this product and 3 g NaOH in 10 ml water and 5 ml EtOH was refluxed for 8 hr. The soln was acidified and evaporated to dryness. The crude diacid **6d** was extracted with ether, the soln dried (Na_2SO_4), and the solvent evaporated to yield 1·57 g (79%). Recrystallization from benzene afforded white amorphous crystals, m.p. 119·0–120·5°; IR ($CHCl_3$) absorption at 5·83 μ.

The dianilide of **6d** crystallized from aq EtOH as small, white needles, m.p. 231·5–232·5°. (Found: C, 75·35; H, 7·39; N, 8·04. $C_{22}H_{26}N_2O_2$ requires: C, 75·39; H, 7·48; N, 8·00%.)

Treatment of **6d** with ethereal diazomethane gave the dimethyl ester; IR ($CHCl_3$) absorption at 5·79 μ; NMR (CCl_4) signals at 6·38 (6H, s), 8·92 and 9·10 τ (6H, s). GLC on a 10-foot PDEAS column (20% on Chromosorb W, 190°) showed only one component (22·0 min).

Mixture of rac-cis- *and* trans-sym-*homopinic acid* (**6b**)

(a) Oxalyl chloride (1·6 g) was added to a soln of 1·0·7 g (0·05 mole) of **8a**[7] in 100 ml anhyd ether containing 2 drops dry pyridine. After 3 hr, the mixture was filtered and the solvent and excess reagent were removed at the aspirator. The residue was then added to an ice-cold soln (300 ml) of diazomethane in ether, prepared from 26 g N-nitrosomethylurea. Concentration of the soln (after 3 hr) gave a yellow oil; IR ($CHCl_3$) absorption at 4·72, 5·80 and 6·11 μ.

Wolff rearrangement of the diazoketone, dissolved in 50 ml EtOH, was performed with the aid of a

silver benzoate-triethylamine catalyst.[21] Distillation of the resulting crude oil gave 8·4 g (66%) of the diethyl ester of racemic **6d**, b.p. 84–85° (0·05 mm); IR (CCl_4) absorption at 5·77 μ.

A mixture containing 0·51 g (2 mmole) of the diethyl ester of *rac* **6d** and 1 g NaOH in 20 ml 50% aq EtOH was refluxed for 1 hr, diluted with 50 ml water and acidified with conc HCl. After addition of excess NaCl, the aq mixture was extracted with ether, and the combined organic layers were dried ($MgSO_4$). Evaporation of the solvent gave 0·23 g (58%) of a waxy solid after trituration with hot pet. ether. Racemic **6d** crystallized from ether–ligroin as clumps of amorphous crystals, m.p. 115·0–115·5°.

Treatment of *rac*-**6d** with ethereal diazomethane gave the dimethyl ester; NMR (CCl_4) signals at 6·40 (6H, s), 8·92, 8·99 and 9·10 τ (6H, s). The intensity of the signals at 8·92 and 9·10 was ca. 2·1 times that of the signal at 8·99.

(b) In the manner previously described,[9] 9·2 g (0·05 mole) of **8d**[8] was allowed to react with 8·7 g morpholine and 3·2 g sulfur. Pure *rac* diacid **6d** separated from ether–ligroin in clusters of almost white needles, m.p. 115·2–116·0°; yield 3·1 g (31%).

The dianilide crystallized from aq EtOH as small, white needles, m.p. 224–227° (lit[8] m.p. 221–223°).

Treatment of *rac*-**6d** with ethereal diazomethane gave the dimethyl ester; IR (CS_2) absorption at 5·77 μ; NMR (CCl_4) signals at 6·38 (6H, singlet), 8·91, 8·99 and 9·09 τ (6H, s). The intensity of the signals at 8·91 and 9·09 was ca. 2·3 times that of the signal at 8·99. GLC on PDEAS (10-foot column, 20% on Chromosorb W, 192°) gave two overlapping peaks (21·0 and 22·3 min) of approximate relative intensity 2·2 to 1·0.

3-*Benzylidene*-6,6-*dimethylbicyclo*[3.1.1]*heptan*-2-*ol* (**12a**)

A soln of 13·8 g (0·1 mole) of **11a**[22] and 10·6 g (0·1 mole) of benzaldehyde in 50 ml 10% NaOH aq and 100 ml 95% EtOH was allowed to stand at room temp for 2 days. The mixture was diluted with 400 ml water and the solid that separated was collected by filtration. One recrystallization from 95% EtOH (100 ml) gave 19·1 g (85%) of **11b**, m.p. 105·5–106·5° (lit[10] m.p. 106–107°), $[\alpha]_D^{26}$ −33·8° ($CHCl_3$).

To an ice-cold soln of 11·3 g (0·05 mole) of **11b** in 500 ml dry ether was added 3·8 g LAH. After the mixture had stirred at 0° for 8 hr, the excess LAH and aluminum complexes were destroyed by cautious addition of sat Na_2SO_4, anhyd Na_2SO_4 was added, and the mixture filtered. Removal of the solvent from the dry ($MgSO_4$) filtrate gave 10·9 g (96%) of crude **12a**; IR ($CHCl_3$) absorption at 2·70, 2·86 and 6·26 μ; UV λ_{max} 254 mμ (ε 16,500), 260 mμ (ε 17,000) and 268 mμ (shoulder, ε 12,000).

The 3,5-*dinitrobenzoate* of **12a** crystallized from acetone as small, almost colorless needles, m.p. 137° dec. (when placed in an oil bath at 135° whose temp was allowed to rise ca. 5° per min); $[\alpha]_D^{26}$ −35·6° ($CHCl_3$). (Found: C, 65·29; H, 5·29; N, 6·75. $C_{23}H_{22}N_2O_6$ requires: C, 65·39; H, 5·25; N, 6·63%)

2-*Acetoxy*-6,6-*dimethylbicyclo*[3.1.1]*heptan*-3-*one* (**12b**)

A soln of 4·56 g (0·02 mole) of crude **12a** and 2·3 g Ac_2O in 10 ml dry pyridine was heated (steam bath) for 2 hr. Enough ice-water was added to the cooled mixture to form an emulsion which was stirred for 1 hr at 0°. An equal vol of water was added and the mixture extracted with CH_2Cl_2. The combined organic layers were washed with cold 5% HCl, cold sat. $NaHCO_3$ aq, and then water, dried (Na_2SO_4), and the solvent removed. Distillation of the residue gave 3·47 g (64%) of the acetate of **12a**, b.p. 116° (0·06 mm), $[\alpha]_D^{26}$ −68·8° ($CHCl_3$); IR ($CHCl_3$) absorption at 5·80 and 6·25 μ; UV λ_{max} 253 mμ (ε 15,700), 260 mμ (ε 16,000), and 267 mμ (shoulder, ε 11,200); NMR (CCl_4) signals at 2·64 (5H, m), 3·39 (1H, m), 4·12 (1H, m), 7·96 (3H, s), 8·74 and 8·95 τ (6H, s).

Ozone-rich oxygen was passed into a chilled (ca. −78°) soln of 6·4 g of the above acetate in 20 ml Me until the blue color of dissolved O_3 just appeared. The mixture was flushed briefly with N_2 and was hydrogenated over 10% Pd-C with external cooling. After filtration of the catalyst, the solvent was evaporated and the residue distilled. The distillate, b.p. 72–77° (0·04 mm), was chilled and a solid isolated. When recrystallized from pet. ether it gave 0·33 g (7%) of rhomboids. Sublimation (45°, 0·05 mm) afforded **12b**, m.p. 95·5–96·5°; IR ($CHCl_3$) absorption at 5·75 and 5·79 μ. (Found: C, 66·59; H, 8·24. $C_{11}H_{16}O_3$ requires: C, 67·32; H, 8·22.)

Isonopinone (6,6-*dimethylbicyclo*[3.1.1]-*heptan*-3-*one*, **7**)

(a) A mixture containing the dimethyl ester of *cis-syn*-**6d**, formed by the action of diazomethane on 400 mg of the diacid, 50 mg of Na shot, and 6 ml of *m*-xylene was heated at 195° (sealed tube) for 40 hr under N_2. The solvent was removed and the residue washed with ether. Acidification of the resulting tan solid with 2N HCl afforded 0·20 g of a viscous, yellow oil which turned red with $FeCl_3$. Hydrolysis of the oil in a refluxing mixture of EtOH (0·5 ml) and 5% H_2SO_4 aq (2 ml) gave a yellow liquid that formed

a minute amount of a deep yellow 2,4-dinitrophenylhydrazone. TLC of the derivative on silica gel (1:1 EtOAc-cyclohexane as the elutant) showed a single spot (R_f 0·80).

(b) By the method of Chapman *et al.*,[11] 98 mg of **12b**, dissolved in 5 ml anhyd THF, was allowed to react with a soln of 0·6 g Ca metal in 50 ml liq NH_3. An excess EtOH was used to consume the residual calcium. The crude product (25 mg), which exhibited IR ($CHCl_3$) absorption at 2·81 and 2·96 μ, was oxidized by the dropwise addition of 0·045 ml of standardized $CrO_3 \cdot H_2SO_4$ reagent[23] to an ice-cold, stirred soln in 5 ml acetone. Recovery of the neutral organic product by extraction with ether gave a clear, yellow liquid, IR ($CHCl_3$) absorption at 5·86 μ. The 2,4-dinitrophenylhydrazone of this preparation of 7 crystallized from dilute EtOH as deep yellow plates, m.p. 161·5–162·5° (lit[14] m.p. 162°). TLC of the derivative on silica gel (1:1 EtOAc-cyclohexane as the elutant) gave a single spot (R_f 0·78).

(c) The previously described procedure[13] for the decarbonylation of **13a**[12] was modified by the use of commercial 5% Pd–$BaSO_4$ in place of $Pd(OH)_2$–$BaSO_4$ to give pure **13b** in 34% yield. Hydration of **13b** (24·4 g, 0·2 mole) by the hydroboration method was conducted as described for α-pinene (**2**).[24] The combined ether extracts (150 ml) containing the crude alcohols were evaporated to ca. 50 ml and the soln was allowed to react, in the manner described,[25] with a chromic acid soln prepared from 20·0 g of sodium dichromate dihydrate and 15 ml 96% H_2SO_4 diluted to 100 ml. After the combined organic layers (100 ml) were dried ($MgSO_4$), the solvent was carefully removed. Distillation of the residue gave 18·9 g (68%) of a white, semi-crystalline material, b.p. 76–77° (10 mm); IR ($CHCl_3$) absorption at 5·83 μ. GLC on an 8-foot DEGS column (20% on Chromosorb W, 158°) gave two peaks (6·2 and 8·1 min) of approximate relative intensity 7·2 to 1·0 (an authentic sample of **11a** gave a retention time of 8·4 min). Two redistillations through an 18-inch Nester and Faust semimicro spinning-band column afforded 7·94 g of white crystalline **7**, b.p. 75·5° (10 mm) [(lit[14] b.p. 85° (10 mm)], m.p. 36·5–37·5° (lit[15] m.p. 40–41°), which was 98% pure by GLC assay as per above. The 2,4-dinitrophenylhydrazone crystallized from aqueous EtOH as deep yellow plates, m.p. 162–163° (lit[14] m.p. 162°), and gave an undepressed mixture m.p. with the 2,4-DNPH of **7**, prepared from **12b**.

The *semicarbazone* of **7** crystallized from EtOAc in small needles, m.p. 187–188°. (Found: C, 61·29; H, 8·90; N, 21·72. $C_{10}H_{17}N_3O$ requires: C, 61·51; H, 8·78; N, 21·52%.)

3,6,6-*Trimethylbicyclo*[3.1.1]*heptan*-3-*ol* 3,5-*dinitrobenzoate* (**14b**)

To a chilled (ca. −78°), stirred soln of 0·15 mole of MeLi[26] in 200 ml ether was added 5·52 g (0·04 mole) of 98% pure **7** dissolved in 5 ml anhyd ether. The Dry Ice–acetone bath was removed after 15 min and the reaction mixture stirred for an additional 3 hr. Sat $Na_2S_2O_3$ aq (5 ml) was added dropwise, with external cooling, and then 10 ml water. The organic layer was separated, washed with three 25-ml portions of sat NaCl aq and dried over $MgSO_4$. After careful distillation of the solvent, the residue was taken up in 20 ml anhyd THF and 8 ml dry pyridine. To the cold (0°) mixture was added a soln of 9·2 g of freshly distilled 3,5-dinitrobenzoyl chloride in 20 ml dry THF. After 24 hr at room temp, the deposit of pyridine hydrochloride was separated, the filtrate poured into 200 ml ice-water, and the resulting ppt collected. Recrystallization from EtOH gave 5·26 g (38%) pure **14b**, m.p. 136·5–137·0° dec.; IR ($CHCl_3$) absorption at 5·80, 6·49 and 7·46 μ; NMR ($CDCl_3$) signals at 0·62 (3H, m), 8·07 (3H, s), 8·72 and 9·02 τ (6H, s). (Found: C, 58·45; H, 5·78; N, 8·25. $C_{17}H_{20}N_2O_6$ requires: C, 58·61; H, 5·79; N, 8·04%.)

3,6,6-*Trimethylbicyclo*[3.1.1]*heptan*-3-*ol* (**14a**)

When 0·12 g LAH was added to a stirred soln of 348 mg (1 mmole) of **14b** in 10 ml anhyd THF, an immediate vigorous reaction occurred. After 5 hr, the excess LAH and aluminum complexes were destroyed (cautious addition of a minimal amount of sat Na_2SO_4 aq), anhyd Na_2SO_4 was added, and the mixture filtered. The filtrate was passed through alumina (10 g, Woelm, neutral, grade I) and the solvent carefully distilled from the collected fractions. Sublimation (45°, 1 atm) of the crude product (77 mg) afforded pure **14a**, m.p. 65–66° (sealed capillary); IR (CCl_4) absorption at 2·75 and 2·87 μ; NMR (CCl_4) signals at 8·57 (3H, s), 8·76 and 8·95 τ (6H, s). (Found: C, 77·76; H, 11·58. $C_{10}H_{18}O$ requires: C, 77·87; H, 11·76%.)

Racemic "orthodene" (3,6,6-*trimethylbicyclo*[3.1.1]-*heptene*-2, **1**) *and* 3-*methylene*-6,6-*dimethylbicyclo*-[3.1.1]*heptane* (**15**)

A flask containing 3·48 g (0·01 mole) of **14b** was heated to 140° under reduced press (100 mm) for 45 min. The liquid formed was flamed gently into a chilled receiver (−75°). During the next 45 min the temp of the oil bath was raised slowly to 180°. The resulting clear, colorless liquid amounted to 1·36 g (100%); NMR (CCl_4) signals at 4·07 (1H, m) and 5·08 τ (2H, m) with a relative intensity of 1·0 to 2·0, respectively. GLC

on an 8-ft diisodecyl phthalate column (10% on Chromosorb W, 116°) showed two peaks (6·6 and 8·6 min) of relative intensity 1·0 to 1·0.

A total of 4·0 g (100%) of mixed olefins was collected on pyrolysis of 10·02 g of **16b**. The mixture was separated by preparative GLC on a 15-ft didecyl phthalate column (15% on Chromosorb W, 122°) with an overall recovery of 88%. Purified racemic **1** had the following properties: b.p. 155·5–156·0° (746 mm), n_D^{20} 1·4672, n_D^{30} 1·4626; d_4^{20} 0·8598; IR (CS_2) absorption at 6·06, 7·30, 7·39, 12·12, 12·50 and 12·94 μ; NMR (CCl_4) signals at 4·03 (1H, m), 8·30 (3H, s), 8·72 and 9·15 τ (6H, s). GLC on an 8-ft diisodecyl phthalate column (10% on Chromosorb W, 109°) showed a single peak (7·8 min). (Found: C, 88·03; H, 11·94. $C_{10}H_{16}$ requires: C, 88·16; H, 11·84%.) For admittedly impure natural "orthodene", the following physical constants were reported:[3] b.p. 168–170° (757 mm), n_D^{30} 1·4670, $[\alpha]_D^{29}$ + 32·60°, d_4^{30} 0·8430.

The isomeric olefin **15** was found to have the following properties: b.p. 162·0–162·5° (746 mm), n_D^{20} 1·4754, n_D^{30} 1·4709; d_4^{20} 0·8641; IR (CS_2) absorption at 3·28, 6·14, 7·29, 7·38, 11·30 and 11·40 μ; NMR (CCl_4) signals at 5·05 (2H, m), 8·76 and 9·13 τ (6H, s). GLC on an 8-ft diisodecyl phthalate column (10% on Chromosorb W, 109°) showed a single peak (10·4 min). (Found: Cl 87·95; H, 11·98. $C_{10}H_{16}$ requires: C, 88·16; H, 11·84%.)

Alternative preparation of 3-methylene-6,6-dimethylbicyclo[3.1.1]heptane (**15**)

By reaction with methylenetriphenylphosphorane [prepared from 3·71 g (10·4 mmoles) methyltriphenylphosphonium bromide and 0·45 g NaH] in 200 ml DMSO[27] at 55° for 24 hr, 0·72 g (5·2 mmoles) of **7** was converted to 0·32 g (45%) of chromatographed (10 g, Woelm, basic alumina) and distilled (b.p. 80°, 50 mm) hydrocarbon. The IR and NMR spectral properties and the GLC retention time showed the product to be identical with the sample of **15** prepared above.

Isomerization of olefin **15** *to* rac-"*orthodene*" (**1**)

Treatment of 100 mg (0·74 mmole) of **15** with excess N-lithioethylenediamine in the manner described for the isomerization of **4** to **2**[17] furnished a mixture of **1** and **15** which by GLC analysis (8-ft column, 10% diisodecyl phthalate on Chromosorb W, 110°) showed that the conversion to **1** had gone to 92% completion (peaks with retention times of 7·9 and 10·1 min and relative intensity 11·8 to 1·0, respectively).

2,6,6-*Trimethylbicyclo*[3.1.1]-*heptan-2-ol* 3,5-*dinitrobenzoate* (**16b**) *and its pyrolysis*

In the manner described for the preparation of **16a**, 2·76 g (0·02 mole) of **11a** was treated with MeLi[26] (0·075 mole) and the resulting **16a** allowed to react with 4·6 g (0·02 mole) of freshly distilled 3,5-dinitrobenzoyl chloride in 20 ml anhyd THF and 4 ml dry pyridine. Several recrystallizations of the product from pentane gave 0·63 g (9%) pure **16b**, m.p. 83·5–84·0° dec; IR ($CHCl_3$) absorption at 5·80, 6·46 and 7·44 μ; NMR ($CDCl_3$) signals at 0·67 (3H, m), 8·25 (3H, s), 8·67 and 8·97 τ (6H, s) (Found: C, 58·49; H, 5·98; N, 8·27. $C_{17}H_{20}N_2O_6$ requires: C, 58·61; H, 5·79; N, 8·04%).

Thermal decomposition of dry **16b** was conducted as described for **16b**, and the volatile products were analyzed by GLC on diisodecyl phthalate (10% on Chromosorb W, 108°). Pyrolysis at 85° (15 min) gave a mixture containing 34% of **2** and 43% of **4**; heating at 140° (15 min) resulted in a smaller amount (10%) of **2** and no **4**. The other volatile products were not identified.

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