Tetrahedron. Vol. 29, pp. 1955 to 1959. Pergamon Press 1973. Printed in Great Britain

TRANS-COPLANAR REARRANGEMENTS
THE CONVERSION OF CAMPHOR TO NOPINONE[1]

J. V. PAUKSTELIS[2] and B. W. MACHARIA[3]
Chemistry, Kansas State University, Manhattan, Kansas 66506

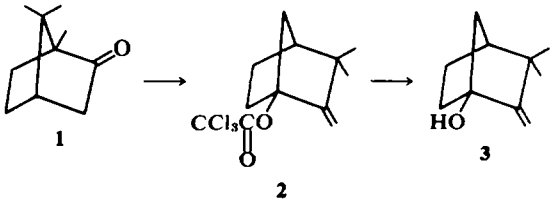
(*Received in the USA* 28 *September* 1972; *Received in the UK for publication* 23 *February* 1973)

Abstract—The conversion of camphor to nopinone was carried out by rearrangement of appropriate glycol monomesylate in a sterospecific manner. The glycol monomesylates were prepared by reaction of camphor and trichloroacetic anhydride to give 1-trichloroacetoxycamphene (**2**) which on hydrolysis and acylation gave 1-acetoxycamphene (**5**). Ozonolysis, selective reduction of **6** and conversion to the mesylate gave 1-acetoxy-3,3-dimethylbicyclo[2.2.1]-hept-*endo*-2-yl mesylate (**10**) which was rearranged to nopinone.

The conversion of pinane monoterpenes to the camphor family by carbonium ion mechanisms has been investigated extensively.[4,5] These investigations led to valuable structural correlations in terpene chemistry and opened up the then new area or carbonium ion chemistry. It is significant that the reverse transformation has been observed infrequently and only under strenuous conditions such as the Bamford-Stevens rearrangement.[6,7] A similar rearrangement under solvolytic conditions[8] is not synthetically useful since the yield of bicyclo-[3.1.1.]heptane products was less than 9%.

We have developed a sequence of reactions that produces the desired bicyclo[3.1.1]heptane ring system by a stereospecific and extremely mild process.[9] The transformation of a bicyclo[2.2.1]-heptane to a bicyclo[3.1.1]heptane is achieved by rearrangement of a glycol monotosylate in a *trans*-coplanar manner. In this report the conversion of camphor to nopinone by three related sequences of reactions is described.

Camphor (**1**) was converted to 1-trichloracetoxy-camphene (**2**) in 20% yield as previously described.[10] The reaction was followed by NMR spectroscopy to minimize any undesired by-products. The reaction seems to proceed as described with one exception: an isomeric camphene could be detected by NMR during the course of the reaction which we assumed was **4** (R = CCl_3CO^-). Hydrolysis of **2** yielded 1-hydroxycamphene (**3**), a known substance,[10,11] which could be acetylated with acetic anhydride to give **5**. The presence on an acetyl group and a terminal methylene group were confirmed by IR $\nu_{max}^{CCl_4}$ 1740, 888 cm^{-1} and NMR (CCl_4) τ 8·00 (acetyl) and 5·43 and 5·32 (unequivalent hydrogens of the methylene group). Ozonolysis in methyl alcohol at −78° followed by reduction of the ozonide with dimethylsulfide[12] gave ketone **6** in 94% yield. The ketone (**6**) was reduced with lithium aluminum tri-t-butoxyhydride



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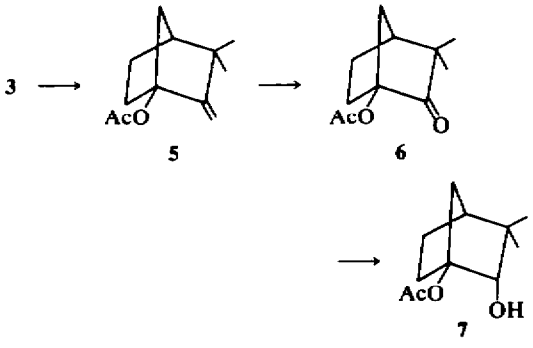

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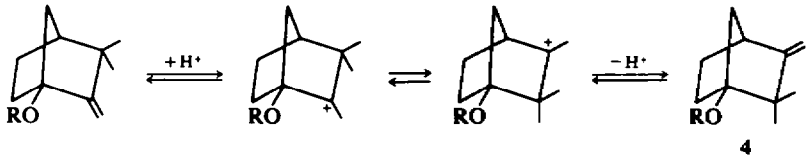
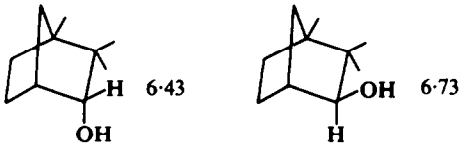
in THF in 67% yield to give 1-acetoxy-3,3-dimethylbicyclo[2.2.1]heptane-*endo*-2-ol (**7**). The



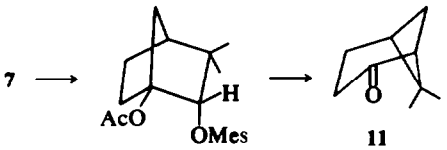
4

endo-hydroxyl configuration for **7** was deduced by comparison of chemical shifts of model compounds **8** and **9**[13] and by parallel syntheses of nopinone that follow. The chemical shift for the *exo*-H of **7** was τ 6·38, very close to the chemical shift of a similar hydrogen of **8**. The acetoxyalcohol **7** was converted to the acetoxymesylate **9** and treated with sodium methoxide in methyl alcohol to give nopinone (**11**)



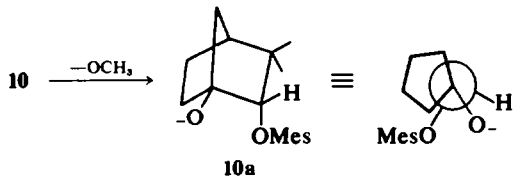
8 **9**

as determined by comparison to an authentic sample prepared from β-pinene. The GLPC retention times of synthetic material and an authentic sample were identical and the infrared spectra and NMR spectra were superimposable, thus completing the conversion of camphor to nopinone.



10 **11**

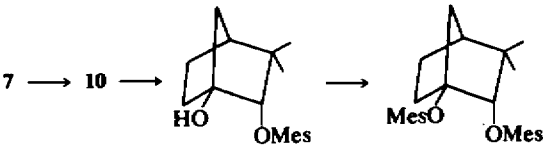
The key step involves attack of methoxide to produce methyl acetate and **10a** which could in a concerted manner result in the migration of the 1,6-bond or the 1,7-bond. If the mesylate is in fact *endo* as indicated, only the 1,7-bond is reasonably *trans*-coplanar to the mesylate as shown by the



10a

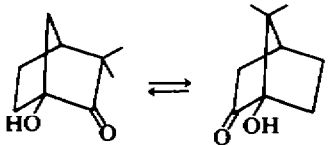
Newman projection of the 1,2-bond and the 1,7-bond should be the only bond that can migrate. All of our results were consistent with that assumption and nopinone was the *only* product detected from the rearrangement.

The only problem encountered in the above sequence was the formation of **10**. Reaction of **7** with methanesulfonyl chloride in pyridine resulted in the desired mesylate (70%) and a dimesylate **12**. The formation of **12** can be rationalized if attack of chloride ion on **10** results in the formation of acetyl chloride and 1-hydroxy-3,3-dimethylbicyclo[2.2.1]-hept-*endo*-2-yl mesylate which can react with another mole of methanesulfonyl chloride to yield the dimesylate (**12**). Several changes in the conditions improved the yield of **10** but did not eliminate the formation of **12**.[9]



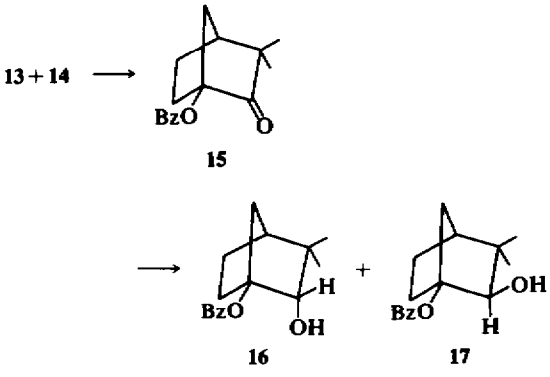
12

A parallel sequence of reaction was initiated to eliminate the formation of the dimesylate **12** starting with the hydroxy ketone **13**. The ketone **13** has been shown to exist in a mobile equilibrium with **14**[14] but treatment of the equilibria mixture with benzyl chloride gives **15** in 90% yield. Reduction



13 **14**

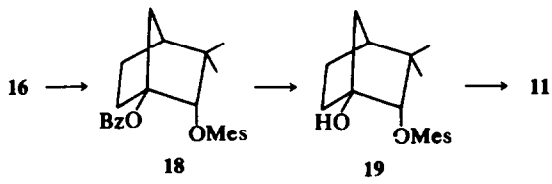
with sodium borohydride gave two isomeric diols in 3:7 ratio, **16** and **17**, which could be readily separated by chromatography on alumina. The major product exhibited a singlet at τ 6·42 and the minor compound τ 6·68 while the model compounds **8** and **9** *endo*-OH and *exo*-OH, were found at τ 6·43 and 6·73 respectively. The *endo*-alcohol **16** was



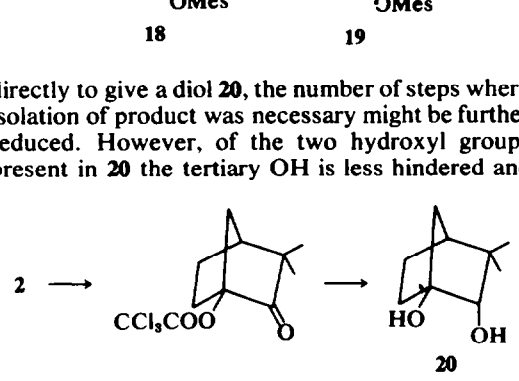
15 **16** **17**

converted to the mesylate **18** (95% yield), debenzylated[15] with Pd—C ethanol, and rearranged with potassium t-butoxide and in t-butyl alcohol at room temperature for five minutes to give nopinone in quantitative yield.[16] No other volatile products were detected by gas-liquid partition chromatography. The overall yield from **2** was greater than 40% and from camphor about 10%.

If **2** were treated with ozone and the ozonide were to be reduced with sodium borohydride



directly to give a diol **20**, the number of steps where isolation of product was necessary might be further reduced. However, of the two hydroxyl groups present in **20** the tertiary OH is less hindered and



reacts more rapidly with reagents such as methanesulfonyl chloride and pivaloyl chloride. Thus a direct conversion to **19** was not possible. The formation of the 1-pivaloxy derivative followed by reaction with methanesulfonyl chloride produced some dimesylate **12** thus making this route no better than the one proceeding through the acetate **10**.

The stereospecific rearrangement of **10** and **11** to nopinone provides a convenient and readily accessible route to many bicyclo[3.1.1]heptane-2-one ring systems from the more available bicyclo[2.2.1]-heptane derivatives. This synthesis serves as a model for the synthesis of bergonotene[17–19] and also points out the differences between solvolytic rearrangements[8] and stereospecific pinacol-type rearrangement in bicyclic systems.

EXPERIMENTAL

Preparation of 1-*trichloroacetoxy*-2-*methylene*-3,3-*dimethylbicyclo*[2.2.1]*heptane* (**2**). The procedure of Mazur *et al.*,[10] was used with the following modifications. The reaction was conducted at 180–185° and was monitored with drawing small samples and examining them by NMR which showed two singlets at τ 5·28 and τ 5·10 for the olefinic protons in 1-trichloroacetoxy-2-methylene-3,3-dimethylbicyclo[2.2.1]heptane in the early part of the reaction. When another pair of singlets at τ 5·4 and τ 5·25 began to appear the reaction was stopped. The reaction time varied between 1·5 and 2·0 hr. Isolation was accomplished as described,[10] and gave **2**: b.p. 87–90° (0·05 mm) 20% yield [lit.[10] b.p. 178–179° (40 mm), 19% yield]; NMR (CCl_4) 8·87 (s, 6, *gem*-dimethyl), 8·8–8·2 (m, 7), 5·28 (s, 1, olefinic) 5·10 (s, 1, olefinic). Attempts to discourage what was presumed to be a products from Nametkin rearrangement by use of magnesium, pyridine, quinoline or sodium hydride were unsuccessful.

Hydrolysis of 1-*trichloroacetoxy*-2-*methylene*-3,3-*dimethylbicyclo*[2.2.1]*heptane* (**2**). The procedure described by Mazur *et al.*,[10] was followed to give **2** in 80% yield.

1-*Acetoxy*-2-*methylene*-3,3-*dimethylbicyclo*[2.2.1]*heptane* (**5**). A soln of **3** (4·5 g; 29·5 mmol) in 17·0 ml pyridine was treated with 12·0 ml Ac_2O and heated on a steam bath for 10 hr. The reaction was cooled, diluted with water, made acidic with 10% HCl and extracted with ether to give an oil which was chromatographed on a silica gel column (133 g). Elution with 3% ether-hexane gave an oil which on distillation gave **5** (5·3 g, 93% yield): b.p. 40–45° (0·2 mm) {lit.[20] 115–118° (31·0 mm)]; IR (neat) 3075 (C=CH_2), 1740 (C=O), 1660 (C=C), 888 cm^{-1} (C=CH_2); NMR (CCl_4) τ 8·92 (s, 6, *gem*-dimethyl), 8·00 (s, 3, acetate), 8·5–7·8 (m, 7), 5·43 (s, 1, olefinic), 5·32 (s, 1, olefinic); mass spectrum *m/e* (rel. intensity) 194 (M^+, 4), 152 (16), 151 (8), 123 (7), 109 (55), 81 (9), 58 (47), 44 (100), 43 (94). (Found: C, 73·92; H, 9·39. Calcd. for $C_{12}H_{18}O_2$: C, 74·19; H, 9·39%.)

1-*Acetoxy*-3,3-*dimethylbicyclo*[2.2.1]*heptan*-2-*one* (**6**). A soln of **5** (1·94 g; 10·0 mmol) in 30 ml MeOH was cooled in a Dry Ice-acetone bath to −78°. Oz was passed through the soln for 40 min after the blue color due to the excess Oz developed. The cold soln was purged with N_2 for 0·5 hr, before 2·0 ml of dimethyl sulfide was added. The reaction was allowed to warm up to room temp and stirred for 5 hr. The excess dimethyl sulfide and the solvent were removed on a rotary evaporator and the residue dissolved in hexane, washed with water twice, and dried ($MgSO_4$). Removal of the solvent at reduced pressure, gave a residue which was distilled b.p. 83–86° (1·0 mm) [lit.[20] m.p. 54–55°] to provide **6** (1·85 g; 94% yield) which had the following properties: IR (CCl_4) 1776, 1754, 1391, 1374 cm^{-1}; NMR (CCl_4) τ 8·98 (s, 3, Me), 8·88 (s, 3, Me), 8·0–8·5 (m, 6), 9·98 (s, 3, acetate), 7·1–7·4 (m, 1), high resolution mass spectrum *m/e* 196 (M^+), base peak 43. Calcd. mass 196·1104; Found: 196·1099.

Reduction of 1-*acetoxy*-3,3-*dimethylbicyclo*[2.2.1]-*heptan*-2-*one* (**6**) *with lithium tri-t-butoxyaluminum hydride*. To a soln of 300 mg (41·2 mmol) of lithium tri-t-butoxyaluminum hydride[21] in 20 ml THF was added a 100 mg (0·5 mmol) of 1-acetoxy-3,3-dimethylbicyclo-[2.2.1]heptan-2-one in 10 ml THF and heated under reflux for 1 hr. The reaction was quenched with water, filtered, the solvent evaporated, the residue dissolved in ether, washed with water, dried ($MgSO_4$) and the ether removed under reduced pressure. Distillation of the residue gave a compound b.p. 65° (0·15 mm) in 80% yield. It was shown by GLPC to consist of the 1-acetoxy-3,3-dimethylbicyclo[2.2.1]heptan-*endo*- and *exo*-2-ols in 84:16 ratio. Analytical sample of the *endo* isomer (**7**) was collected by GLPC and exhibited the following properties: IR (neat) 3640 (O—H), 1742 (C=O), 1718 cm^{-1}; NMR (CCl_4) τ 9·10 (s, 3, Me), 8·93 (s, 3, Me), 8·0–8·6 (m, 7) 7·98 (s, 3, acetate), 6·38 (s, 1, O—C—H), 6·25 (s, 1, OH, exchanges with D_2O). (Found: C, 66·38; H, 9·16. Calcd. for $C_{11}H_{18}O_3$: C, 66·65; H, 9·15%.)

Nopinone from 1-*acetoxy*-3,3-*dimethylbicyclo*[2.2.1]-*hept-endo*-2-*yl mesylate* (**10**). A soln of **7** (400 mg; 2·0 mmol) obtained from chromatography on alumina (Act III, hexane-2% methanol) in 5·0 ml of pyridine was treated with 300 mg (2·63 mmol) of mesyl chloride and left in the freezer (*ca* −21°) for 4 days. After diluting with ether, the precipitated pyridinum hydrochloride was removed by filtration and the excess pyridine was removed azeotropically with toluene. The residue was filtered through a short alumina column to give 500 mg of an oil. The NMR of this sample showed it to be a mixture of two compounds in 30:70 ratio. Attempts to separate them on a longer column were not successful. It was shown that

the NMR resonance not compatable with those expected for **10** were indeed superimposable with those of 1-mesyloxy-3,3-dimethylbicyclo[2.2.1]hept-*endo*-2-yl mesylate.[9] The mixture was treated with 1·0 ml of NaOMe (2·54 M) in MeOH overnight. The MeOH solvent was evaporated under reduced pressure and the residue dissolved in hexane, washed with water, dried ($MgSO_4$) and concentrated to give 300 mg of a liquid from which nopinone (133 mg 85% based on the 30:70 mixture) was isolated by collection from a GLPC. This sample of nopinone had identical retention times on GLPC and identical NMR and IR spectra with an authentic sample prepared from β-pinene.

Hydrolysis of 1-*trichloroacetoxy*-3,3-*dimethylbicyclo*-[2.2.1]*heptan*-2-*one*. A soln of 100 mg (0·336 mmol) of 1-trichloroacetoxy-3,3-dimethylbicyclo[2.2.1]heptan-2-one in 10 ml MeOH was treated with 10 drops of 10% NaOHaq and refluxed for 10 hr. The solvent was removed under reduced pressure, the residue dissolved in hexane and washed with water. After drying ($MgSO_4$), and concentrating under reduced pressure 40 mg (77% yield) of a mixture of 1-hydroxy-3,3-dimethylbicyclo[2.2.1]heptan-2-one and 1-hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-2-one was collected.[14]

1-*Benzyloxy*-3,3-*dimethylbicyclo*[2.2.1]*heptan*-2-*one* NaH (1·0 g) in oil was washed 3 times with hexane and covered with 25 ml DMF before the addition of 1·5 g (10, 0 mmol) of a mixture of 1-hydroxy-3,3-dimethylbicyclo[2.2.1]heptan-2-one and 1-hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-2-one dissolved in 10 ml DMF. Vigorous evolution of H_2 occurred and after it subsided 5·0 ml (44·0 mmol) of benzyl chloride in 10 ml DMF was added and the mixture was stirred at room temp for 24 hr. Extraction with ether, drying ($MgSO_4$) and concentrating on a rotary evaporator gave a brown oil which contained in addition to dibenzyl ether, two other components. The crude mixture was chromatographed on a silica gel column (50 g). After removal of the initial fractions containing the unreacted benzyl chloride and dibenzyl ether, 1·25 g (57% yield) of an oil was obtained from the fractions eluted with 4% ether-hexane. Analytical sample was collected on GLPC and exhibited the following spectral properties: IR (neat) 1740 (C=O), 1380, 1360 (*gem*-dimethyl), 740, 700 cm^{-1}; NMR (CCl_4) τ 8·96 (s, 6, *gem*-dimethyl), 8·4–7·9 (m, 7), 5·46 (s, 2, benzylic), 2·75 (br s, 5, aromatic); mass spectrum *m/e* (rel. intensity) 244 (M^+, 2), 216 (12), 125 (50), 97 (8), 92 (40), 91 (100), 83 (50), 69 (40), 65 (15), 55 (60), 41 (16). (Found: C, 78·70; H, 8·35. Calcd. for $C_{16}H_{20}O_2$: C, 78·65; H, 8·25%.)

The structure of this compound was based on the fact that the Me's appeared as a singlet at τ 8·96 which implied they were influenced equally by the CO. On that basis it was assigned 1-benzyloxy-3,3-dimethylbicyclo-[2.2.1]heptan-2-one.

Elution with ether gave another 500 mg of (23%) of a mixture of 1-benzyloxy-3,3-dimethylbicyclo[2.2.1]heptan-2-one and another compound in a ratio of 6:1. The compound was collected by GLPC and exhibited the following properties: IR (neat 1740 (C=O), 1380, 1360 (*gem*-dimethyl), 700 cm^{-1} (monosubstituted benzene); NMR (CCl_4) τ 9·00 (s, 3, Me), 8·89 (s, 3, Me), 8·8–7·3 (m, 7), 5·16 (AB, 2, J = 12 Hz, benzylic), 2·7 (s, 5, aromatic).

This compound was assigned to 1-benzyloxy-7,7-dimethylbicyclo[2.2.1]heptan-2-one on the basis of the two singlets at τ 9·00 and τ 8·89 attributable to two different Me groups. Further reactions confirmed the structural assignments.

1-*Benzyloxy*-3,3-*dimethylbicyclo*[2.2.1]*heptan*-endo *and* exo-2-*ol* (**16** and **17**). To a soln of 1·2 g (5·0 mmol) of 1-benzyloxy-3,3-dimethylbicyclo[2.2.1]heptan-2-one in 25 ml of 95% EtOH was added dropwise a soln of $NaBH_4$ (600 mg) in 10 ml EtOH. After stirring for 12 hr, the solvent was removed on a rotary evaporator, the residue acidified with 10% HCl, extracted with ether, dried ($MgSO_4$) and concentrated to give 1·10 g of a yellow oil which was chromatographed on an alumina column (Act III, 20 g). Elution with hexane gave 300 mg (25% yield) of **17** as deduced from the following data: IR (neat) 3500 (bonded OH), 1380, 1365 (*gem*-dimethyl), 700 cm^{-1} (monosubstituted benzene); NMR (CCl_4) τ 9·0 (s, 3, Me), 8·99 (s, 3, Me), 8·8–7·6 (m, 7), 6·68 (br s, 1, O—C—H), 5·50 (s, 2, benzylic, 2·70 (s, 5, aromatic), high resolution mass spectrum *m/e* 246 (M^+). Calcd. mass 246·1614; Found 246·1603.

Elution with hexane-benzene gave 700 mg (59% yield) of a solid **16**: m.p. 47–48°; IR (CCl_4) 3600 (free OH), 1380, 1365 (*gem*-dimethyl, 725, 700 cm^{-1} (mono-substituted benzene); NMR (CCl_4) τ 9·17 (s, 3, Me), 9·03 (s, 3, Me), 8·7–8·0 (m, 7), 7·77 (s, 1, OH), 6·47 (s, 1, O—C—H), 5·55 (s, 2, benzylic), 2·80 (s, 5, aromatic); mass spectrum *m/e* (rel. intensity) 246 (M^+, 3), 173 (23), 105 (47), 92 (33), 91 (100), 83 (50), 77 (26), 65 (20), 55 (23). Calcd. mass 246·1614; Found: 246·1607.

1-*Benzyloxy*-3,3-*dimethylbicyclo*[2.2.1]*hept*-endo-2-*yl mesylate* (**18**). A mixture of **16** (100 mg; 0·405 mmol) and 100 mg (1·05 mmol) mesyl chloride in 10 ml pyridine was placed in a refrigerator (*ca* −21°) for 21 hr, poured into 10% HCl, extracted 3 times with 10-ml portions of ether, dried ($MgSO_4$), and concentrated on a rotary evaporator. The residue was chromatographed on an alumina column (1·0 g Act I) and eluted with ether. An oil that could not be induced to crystallize was obtained (100 mg, 76%) and exhibited the following spectral properties: IR (neat) 1351, 1176, 1020, 700 cm^{-1}; NMR (CCl_4) τ 9·03 (s, 3, Me), 8·90 (s, 3, Me), 8·4–8·0 (m, 7), 7·19 (s, 3, mesylate), 5·52 (s, 3, benzylic and O—C—H), 2·80 (s, 5, aromatic). The oil was used without further purification.

Nopinone from 1-*hydroxy*-3,3-*dimethylbicyclo*[2.2.1]-*hept*-endo-2-*yl mesylate* (**19**). A soln of 100 mg (0·30 mmol) of 1-benxyloxy-3,3-dimethylbicyclo[2.2.1]hept-*endo*-2-yl mesylate in 10·0 ml of abs EtOH was hydrogenated[87] at atmospheric pressure in the presence of *ca* 20 mg of 5% Pd—C for 0·5 hr. The catalyst was filtered, the solvent removed on a rotary evaporator and the residue passed through an alumina column (Act I, 1·0 g). Elution with 2% MeOH-ether gave an oil which indicated partial rearrangement by the presence of both nopinone and 1-hydroxy-3,3-dimethylbicyclo[2.2.1]hept-*endo*-2-yl mesylate.

The oil was treated with 0·5 ml soln of t-BuOK in t-BuOH (1·5 M) for 4 hr at room temp. The solvent was removed on a rotary evaporator and the residue dissolved in ether and washed twice with water. The organic layer was dried ($MgSO_4$), concentrated and collected by GLPC to give 35 mg (85% yield) of nopinone shown to be identical in all respects (GLPC, NMR, IR) to an authentic sample from β-pinene.

Nopinone from β-*pinene*. A soln of 10·0 g (73·3 mmol) of β-pinene (Aldrich) in 150 ml MeOH was cooled to −78° in a Dry Ice-acetone bath. Oz was bubbled through the soln for 1·5 hr, the soln was purged with N_2 for 0·5 hr

and was treated with 10·0 ml dimethyl sulfide as the temp was allowed to rise. The excess dimethyl sulfide and MeOH were removed on a rotary evaporator and the residue dissolved in hexane. The organic layer was washed with water, dried and concentrated on a rotary evaporator to give 6·5 g (65% yield) of nopinone which was distilled at 110–115° (35·0 mm) [lit.[22] (83–86° (12·0 mm)]. Analytical sample was collected on GLPC and showed the following spectral properties: IR (neat) 1710 (C=O), 1385, 1370 (*gem*-dimethyl), 1200 cm^{-1}; NMR (CCl_4) 9·28 (s, 3, Me), 8·77 (s, 3, Me), 8·6–7·5 (m, 8). This sample was used for spectral comparisons.

3,3-*Dimethylbicyclo*[2.2.1]*heptan*-1-endo-2-*diol* (**20**). A soln of 1·00 g (3·32 mmol) of 1-trichloroacetoxy-2-methylene-3,3-dimethylbicyclo[2.2.1]heptane in 40·0 ml MeOH was treated with Oz at −78° for 1 hr. The cold soln was purged with N_2 for 0·5 hr, treated with a soln of $NaBH_4$ (2·0 g; 51·0 mmol) in 10 ml water with stirring and was allowed to warm up to room temp. After stirring for 24 hr, the excess MeOH was removed under reduced pressure. The residue was diluted with 20 ml water and extracted 3 times with 50-ml portions ether. The combined organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure to give an oil. Trichloroethanol was removed under vacuum with little warming to give a solid which was crystallized from hexane in 80% yield: m.p. 112–113; IR ($HCCl_3$) 3597 (free OH), 3448 (bonded OH), 1109, 1075, 1000, 926 cm^{-1}; NMR ($DCCl_3$) τ 9·15 (s, 3, Me), 8·97 (s, 3, Me), 8·0–8·7 (m, 7), 6·89 (br s, 2, OH), 6·47 (d, 1, $J = 2$ Hz, O—C—H); mass spectrum *m/e* base peak 83. (Found: C, 69·50; H, 10·20. Calcd. for $C_9H_{16}O_2$: C, 69·19; H, 10·32%.)

Since this compound did not have a CO absorption in the IR and had a proton at τ 6·47 with $J = 2$ Hz, its structure was deduced to be **20**. The *endo* stereochemistry was deduced from the chemical shift of the proton bearing the OH, the expected *exo* attack by $NaBH_4$ and the presence of a long range coupling to the 7-anti proton.

1-*Pivaloxy*-3,3-*dimethylbicyclo*[2.2.1]*hept*-endo-2-*yl mesylate*. A soln of 500 mg (3·2 mmol) of 3,3-dimethylbicyclo[2.2.1]heptan-1-*endo*-2-diol in 5·0 ml pyridine was treated with 400 mg (3·3 mmol) pivaloly chloride and allowed to stand at room temp for 6 hr, then poured onto ice-water containing HCl, extracted with ether, dried ($MgSO_4$) and evaporated *in vacuo*. The crude product was treated with 500 mg mesyl chloride in 5·0 ml pyridine for 12 hr, then poured onto ice containing HCl, extracted, dried and the ether removed under reduced pressure. The residue was passed through an alumina column (Act. III) and eluted with hexane to give 200 mg (20% yield) of 1-pivaloxy-3,3-dimethylbicyclo[2.2.1]hept-*endo*-2-yl mesylate: m.p. 101–103° IR (CCl_4) 1724 (C=O), 1370, 1220, 1183, 1156, 971 cm^{-1}; NMR (CCl_4) τ 9·00 (s, 3, Me), 8·85 (s, 12, 4-Me groups), 8·4–7·5 (m, 7), 7·10 (s, 3, mesylate), 5·23 (br s, 1, O—C—H). (Found: C, 56·50; H, 8·40. Calcd. for $C_{15}H_{26}O_5S$: C, 56·58; H, 8·23%.)

Nopinone from 1-*pivaloxy*-3,3-*dimethylbicyclo*[2.2.1]-*hept*-endo-2-*yl mesylate*. To 100 mg (0·32 mmol) of 1-pivaloxy-3,3-dimethylbicyclo[2.2.1]hept-*endo*-2-yl mesylate was added 0·5 ml of NaOMe (2·5 M) at room temp and stirred for 1 hr. The solvent was evaporated and the residue dissolved in ether, washed with water, dried ($MgSO_4$) and concentrated under reduced pressure to give 40 mg (90% yield) on nopinone identical in all respects to an authentic sample prepared from β-pinene.

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[2]Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Research Corporation and the National Science Foundation (GP 15334 for support of this work and for a grant to the Department of Chemistry, Kansas State University and for the purchase of XL-100 and T-60 NMR spectrometers.

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