

## Stable Carbocations. Part 16.<sup>1</sup> Properties of 2-Substituted *exo*-5,6-Trimethylenenorbornan-2-ylum † Ions

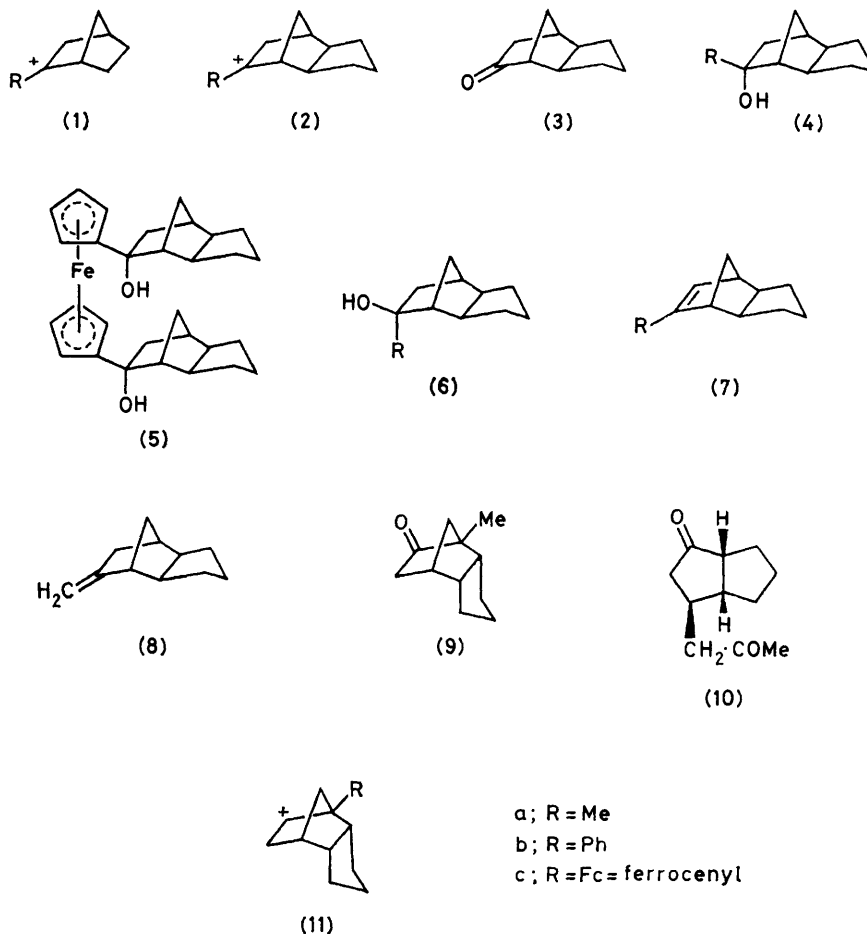
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In formic acid solution, the 2-methyl-*exo*-5,6-trimethylenenorbornan-2-ylum ion gives products resulting from Wagner–Meerwein rearrangement, 3,2-hydride shift, and cation–alkene coupling. Under similar conditions, the 2-phenyl analogue also gives dimeric coupling products, whereas the 2-ferrocenyl analogue is stable. The last-mentioned cation has been obtained in stereoisomeric forms which interconvert in trifluoroacetic acid solution.

In principle, 2-substituted norbornan-2-yl cations (1) may rearrange by three pathways, *viz.* Wagner–Meerwein shift, *exo*-3,2-hydride shift, and *endo*-6,2-hydride shift, each generating a secondary alkylum ion.<sup>2</sup>

strongly acidic media, *e.g.* concentrated formic acid or glacial acetic–sulphuric acid mixtures, and the 2-methyl- (1a)<sup>3</sup> and 2-phenyl-substituted (1b)<sup>4</sup> cations give rearranged products in these solvents. For systems



Although conversion of a tertiary into a secondary carbenium ion is thermodynamically unfavourable in most cases, reaction conditions which permit reversible product formation from the tertiary but not the secondary species often lead to the isolation of a rearranged product. Such conditions are best attained in

† In terms of IUPAC nomenclature this species is more correctly named tricyclo[5.2.1.0<sup>2,6</sup>]decan-8-ylum or hexahydro-4,7-methanoindan-5-ylum.

<sup>1</sup> Part 15, T. S. Abram and W. E. Watts, preceding paper.

<sup>2</sup> G. D. Sargent, *Quart. Rev.*, 1966, **20**, 301.

containing more powerfully electron-donating 2-substituents, however, rearrangement is correspondingly disfavoured; the 2-ferrocenyl-substituted cation (1c), for example, is stable in acidic solutions.<sup>5</sup>

Since fusion of a 5,6-trimethylene bridge to the

<sup>3</sup> S. Beckmann and G. Eder, *Chem. Ber.*, 1958, **91**, 2878; J. Paasivirta, *Annalen*, 1965, **686**, 1; *Acta Chem. Scand.*, 1968, **22**, 2200.

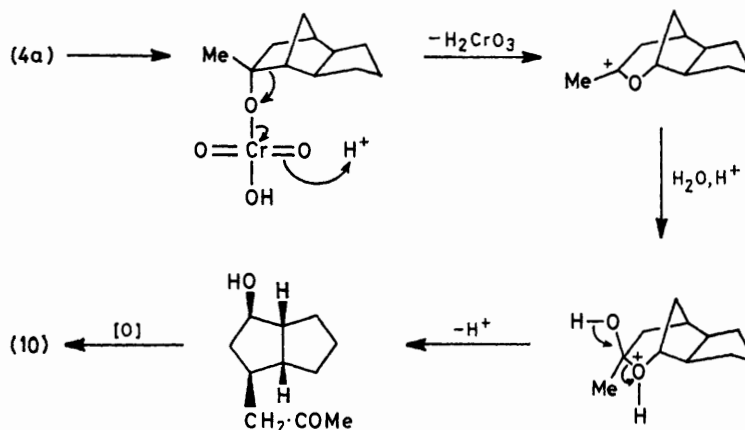
<sup>4</sup> D. C. Kleinfelter and P. von R. Schleyer, *J. Org. Chem.*, 1961, **26**, 3740.

<sup>5</sup> M. J. A. Habib and W. E. Watts, *J. Chem. Soc. (C)*, 1970, 2552.

norbornane structure increases the strain within the system, it seemed possible that the propensity towards rearrangement of a cation of the type (2) might be different from that of its norbornanyl analogue (1). We have investigated this situation by study of the properties of the 2-methyl- (2a), 2-phenyl- (2b), and 2-ferrocenyl-substituted (2c) cations and comparison with those already established<sup>3-5</sup> for their bicyclic counterparts (1a-c).

**Synthetic Methods.**—Treatment of the known<sup>6</sup> ketone (3)\* with methyl-lithium, phenyl-lithium, or lithiated

at 50 °C. To facilitate separation, this mixture was treated with Jones reagent,<sup>9</sup> which oxidises the formates of secondary alcohols to ketones,<sup>10</sup> and the product was chromatographed ( $\text{Al}_2\text{O}_3$ ) giving the alcohols (4a) (35% yield) and (6a) (18%), the ketone (9) (10%), and the diketone (10) (5%). Since the alcohol content of the original mixture was low, the alcohols must arise by hydrolysis of their formates during later treatment. The ketone (9), which was identified spectroscopically (Experimental section), must result from Wagner-Meerwein rearrangement of the first-formed cation (2a),



ferrocene, followed by hydrolysis, gave the appropriate tertiary alcohols (4a-c). From the ferrocene reaction, a small amount of the diol (5) was also isolated. The hydroxy-groups of these products are assigned an *endo*-configuration since nucleophilic addition reactions of bicyclo[2.2.1]heptan-2-ones are known to proceed preferentially from the *exo*-face of the carbonyl group.<sup>7</sup> The *endo*-alcohols (4a-c) were readily converted into their *exo*-epimers (6a-c) by reaction with hydrochloric acid followed by hydrolysis; the intermediate tertiary chlorides were not isolated.

Dehydration of the *endo*-alcohols (4b and c) by the phosphoryl chloride-pyridine method<sup>8</sup> gave the corresponding alkenes (7b and c). Under the same conditions, the alcohol (4a) gave a mixture of the isomeric alkenes (7a) and (8) in the proportions 1 : 4, respectively. This mixture resisted separation and its composition was unaffected following treatment with either hydrogen chloride in chloroform or potassium *t*-butoxide in *t*-butyl alcohol. The pure exocyclic alkene (8) was obtained by a Wittig reaction of the ketone (3) with methylene-triphenylphosphorane.

**The 2-Methyl-substituted Cation (2a).**—A mixture of the same products, mainly formates, in similar proportions, was obtained from reactions of the alcohols (4a) and (6a) and the alkene (8) with 98% formic acid

addition of formic acid to the resulting secondary carbenium ion (11a), and oxidation of the *exo*-formate produced.

The diketone (10) results not from the original formic acid reaction but from the oxidation step. In an independent experiment, the same product was obtained by reaction of the alcohol (4a) with the Jones reagent. Although tertiary alcohols are normally inert to this reagent, in this case reaction of the first-formed chromate is accompanied by relief of strain and by formation of an oxygen-stabilised carbenium ion (Scheme 1).

The reactions of the alcohols (4a) and (6a) with formic acid were repeated at 95 °C. The product was hydrolysed with ethanolic potassium hydroxide and separated chromatographically as before. Irrespective of starting material, there were obtained the alcohol (4a) (24%), a hydrocarbon ( $\text{C}_{22}\text{H}_{32}$ ) (24%), and a secondary alcohol ( $\text{C}_{11}\text{H}_{18}\text{O}$ ) (18%), together with several unidentified minor constituents. The hydrocarbon product, probably a mixture of isomers, most likely results from cation-alkene coupling reactions, *e.g.* addition of (2a) or (11a) to (7a) or (8). The nature of this material, whose <sup>1</sup>H n.m.r. spectrum contained vinylic proton resonances, was not investigated further. The spectroscopic properties (Experimental section) of the secondary alcohol

<sup>7</sup> See J. A. Berson in 'Molecular Rearrangements,' Part 1, Interscience, New York, 1963, p. 130.

<sup>8</sup> K. L. Rinehart and E. G. Perkins, *Org. Synth.*, 1957, **37**, 37.

<sup>9</sup> See A. Bowers, T. G. Halsall, E. R. H. Jones, and A. Lemm, *J. Chem. Soc.*, 1953, 2548.

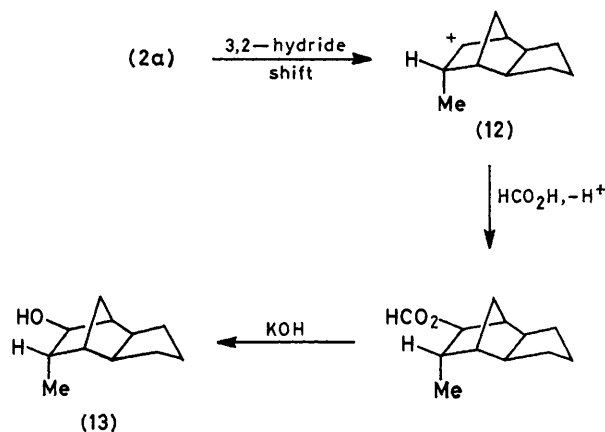
<sup>10</sup> E. J. Corey, M. Ohno, S. W. Chow, and R. A. Scherrer, *J. Amer. Chem. Soc.*, 1959, **81**, 6305.

\* For each of the structures shown in the text, only one stereoisomeric form is depicted. All the compounds were racemic mixtures.

<sup>6</sup> H. A. Bruson and T. W. Reiner, *J. Amer. Chem. Soc.*, 1945, **67**, 723.

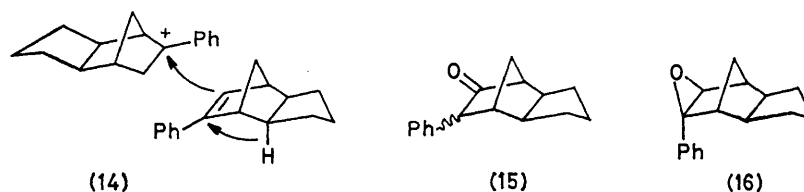
were consistent with the structure (13),\* arising as suggested in Scheme 2.

In hot formic acid solution, therefore, the cation (2a)



SCHEME 2

undergoes both Wagner–Meerwein rearrangement and 3,2-hydride shift to give the secondary carbenium ions (11a) and (12), respectively, which are converted into



SCHEME 3

Acid-catalysed alkene dimerisation becomes significant only at high reaction temperatures. Under similar reaction conditions, the bicyclic cation (1a) gives only

\* The <sup>1</sup>H n.m.r. spectrum of this compound is not consistent with other secondary alcohol structures resulting from rearrangement of (2a) by Wagner–Meerwein shift or by alternative hydride-shift mechanisms (e.g. 6,2- followed by 1,2-shift).

1-methylnorbornan-2-*exo*-yl formate, the product of Wagner–Meerwein rearrangement.<sup>3</sup>

The 2-Phenyl-substituted Cation (2b).—Treatment of either alcohol (4b) or (6b) or the alkene (7b) with 98% formic acid at 70 °C gave a mixture of the same two isomeric hydrocarbons (C<sub>32</sub>H<sub>36</sub>) whose <sup>1</sup>H n.m.r. spectra lacked vinylic proton resonances. As before, these products probably result from cation–alkene coupling [cf. (14)] and their structures were not elucidated. Related dimeric products are formed in formic acid from the cation (1b) which gives mainly 1-phenylnorbornan-2-*exo*-yl formate, the Wagner–Meerwein rearrangement product.<sup>4</sup>

In some of these reactions, but not reproducibly, there were also obtained as by-products two isomeric compounds (C<sub>16</sub>H<sub>18</sub>O). These could not be separated completely but the spectroscopic properties of the mixture indicated the ketone (15) and the epoxide (16) as the constituents. Attempts to prepare the latter by epoxidation of the alkene (7b) with *m*-chloroperbenzoic acid gave instead the hydroxy-ester (17a), formed as indicated in Scheme 3. A similar mechanism has been proposed<sup>11</sup> for the conversion of 2-phenylnorborn-2-ene

into the *exo,cis*-2,3-diol on reaction with performic acid. Hydrolysis of the hydroxy-ester (17a) gave the diol (17b), identical with the product obtained from the alkene (7b) by the osmium tetroxide *cis*-hydroxylation

procedure. In the original reactions, the epoxide (16) is probably formed by autoxidation of the alkene (7b)<sup>12</sup> and is converted into the ketone (15) by acid-catalysed

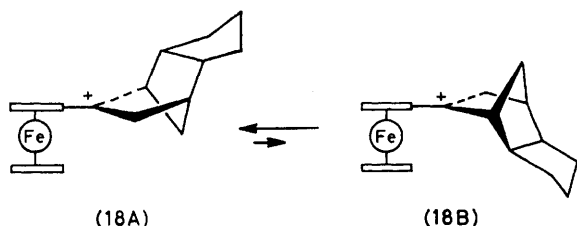
<sup>11</sup> D. C. Kleinfelter and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1961, **83**, 2329.

<sup>12</sup> Cf. R. Huisgen, R. Grashey, and J. Sauer in 'The Chemistry of Alkenes', ed. S. Patai, Interscience, New York, 1964, ch. 11.

rearrangement. We were unable to prepare (15) by pinacol rearrangement of the diol (17b).

**The 2-Ferrocenyl-substituted Cation (2c).**—The alcohols (4c) and (6c) and the alkene (7c) dissolved readily in 98% formic acid. When these solutions were quenched by dilution with water, a mixture of (4c) (34%), (6c) (7%), and (7c) (55%) was obtained, irrespective of starting material. No trace of product resulting from rearrangement of the intermediate cation (2c) was detected. Under the same reaction conditions, a similar mixture of deprotonation and addition products was formed from the 2-ferrocenylbornan-2-ylum ion (1c).<sup>5</sup>

The stability of the cation (2c) in acidic media permitted its observation by <sup>1</sup>H n.m.r. spectroscopy. In



the formation of a ferrocenylalkylium ion by ionisation of a neutral precursor, it is well established<sup>13</sup> that the leaving group prefers to depart in a direction *exo* to the ferrocenyl group, anchimerically assisted by interannular electrons. It is also known<sup>13b</sup> that there exists a significant energy barrier to rotation around the Fe-C<sup>+</sup> bond of such species. Accordingly, dissolution of the alcohols (4c) and (6c) in trifluoroacetic acid gave initially different stereoisomers of the cation (2c), *viz.* (18A) and (18B), respectively, which exhibited distinctive <sup>1</sup>H n.m.r. spectra (Experimental section). Slow rotational equilibration then occurred, giving finally a solution in which the sterically less-congested rotamer (18A) predominated (>95%). Dissolution of the alkene (7c) in trifluoroacetic acid gave a similar equilibrium mixture.

In summary, introduction of an *exo*-5,6-trimethylene bridge apparently reduces the ease with which the cations (1a and b) undergo Wagner-Meerwein shift, the sole rearrangement pathways observed for these bicyclic species. The bicyclic and tricyclic ferrocenylalkylium ions (1c) and (2c) are both stable in acidic media and give similar product mixtures on quenching.

#### EXPERIMENTAL

For general remarks, see Part 4.<sup>13b</sup> Molecular weights were determined by accurate mass measurement of the molecular ion (A.E.I. MS9 mass spectrometer at 70 eV).

**exo-5,6-Trimethylenenorbornan-2-one (3).**—Aqueous chromic acid (8N; 260 ml) was added dropwise over 3 h to a stirred, ice-cooled solution of *exo*-5,6-trimethylenenorbornan-2-yl formate<sup>14</sup> (91 g, 0.5 mol) in acetone (200

ml). The mixture was stirred for a further 16 h and then poured into water (1 000 ml) containing sodium sulphite (2.5 g). The solution was extracted thoroughly with ether, and the combined extracts were washed (H<sub>2</sub>O), dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated. The residue was distilled under reduced pressure giving the ketone (3) (62 g, 82%), a viscous liquid, b.p. 108–110° at 20 mmHg (lit.,<sup>6</sup> 130–132° at 29 mmHg) (Found: C, 79.6; H, 9.2. Calc. for C<sub>10</sub>H<sub>14</sub>O: C, 80.0; H, 9.3%);  $\nu_{\max}$ . (film) 1 745 cm<sup>-1</sup> (CO);  $\tau$  (CDCl<sub>3</sub>) 7.6–9.2 (m).

**2-*exo*-Methyl-*exo*-5,6-trimethylenenorbornan-2-ol (4a).**—A mixture of iodomethane (17 g, 0.12 mol) and the ketone (3) (15 g, 0.10 mol) was added dropwise over 2 h to a stirred, ice-cooled suspension of lithium chips (1.76 g, 0.25 g atom) in dry ether (200 ml). The mixture was stirred overnight and then methanol (50 ml) was added cautiously. The solution was poured into water (1 000 ml) and the organic layer was separated and combined with two ethereal extracts of the aqueous layer. The total extract was washed (H<sub>2</sub>O), dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated, and the residue was dissolved in light petroleum and chromatographed (Al<sub>2</sub>O<sub>3</sub>). Light petroleum eluted unchanged ketone (2.5 g, 17% recovery). Light petroleum-ether (4 : 1) eluted the alcohol (4a) (13.5 g, 81%), needles, m.p. 83–84° (from light petroleum) (lit.,<sup>15</sup> 81.5–82°) (Found: C, 79.5; H, 10.8%; M, 166.1369. Calc. for C<sub>11</sub>H<sub>18</sub>O: C, 79.5; H, 10.8%; M, 166.1358);  $\nu_{\max}$ . (CCl<sub>4</sub>) 3 620 and 3 500–3 300 cm<sup>-1</sup> (OH);  $\tau$  (CDCl<sub>4</sub>) 7.42 (1 H, q, bridgehead proton), 8.70 (3 H, s, Me), and 7.9–9.3 (14 H, m, remaining protons).

**2-*exo*-Phenyl-*exo*-5,6-trimethylenenorbornan-2-ol (4b).**—A mixture of bromobenzene (17.5 g, 0.11 mol) and the ketone (3) (15 g, 0.10 mol) was added dropwise over 2 h to a stirred, ice-cooled suspension of lithium chips (1.8 g, 0.26 g atom) in dry ether (150 ml). The mixture was stirred overnight, and the product was extracted as in the preceding experiment and chromatographed (Al<sub>2</sub>O<sub>3</sub>). Light petroleum-ether (3 : 2) eluted the alcohol (4b) (18.5 g, 82%), needles, m.p. 73–74° (from light petroleum) (lit.,<sup>15</sup> 73.4–74.6°) (Found: C, 84.1; H, 8.8%; M, 228.1511. Calc. for C<sub>16</sub>H<sub>20</sub>O: C, 84.2; H, 8.8%; M, 228.1514);  $\nu_{\max}$ . (CCl<sub>4</sub>) 3 598 cm<sup>-1</sup> (OH);  $\tau$  (CDCl<sub>3</sub>) 2.3–2.8 (5 H, m, Ph), 7.22 (1 H, q, bridgehead proton), and 7.5–9.3 (14 H, m, remaining protons).

**2-*exo*-Ferrocenyl-*exo*-5,6-trimethylenenorbornan-2-ol (4c).**—A solution of ferrocene (37 g, 0.20 mol) in dry tetrahydrofuran (100 ml) was added to a solution of *n*-butyl-lithium (0.23 mol) in ether-hexane (1 : 1; 200 ml), and the mixture was stirred for 6 h. A solution of the ketone (3) (30 g, 0.20 mol) in dry tetrahydrofuran (50 ml) was then added and the mixture was stirred overnight. The reaction was worked up as in the previous experiments and the product was chromatographed (Al<sub>2</sub>O<sub>3</sub>). Light petroleum eluted unchanged ferrocene (13 g, 35% recovery). Light petroleum-ether (3 : 2) eluted the alcohol (4c) (24 g, 36%), yellow needles, m.p. 98–100° (from light petroleum) (Found: C, 71.4; H, 7.2. C<sub>20</sub>H<sub>24</sub>FeO requires C, 71.4; H, 7.1%);  $\nu_{\max}$ . (CCl<sub>4</sub>) 3 560 cm<sup>-1</sup> (OH);  $\tau$  (CDCl<sub>3</sub>) 5.65–5.9 (9 H, m + s, ferrocenyl), 7.2 (1 H, q, bridgehead proton), 7.73 (1 H, s, OH), and 7.8–9.3 (13 H, m, remaining protons). Light petroleum-ether (1 : 4) eluted (5) (2 g, 2%), a yellow

<sup>13</sup> (a) E. A. Hill and J. H. Richards, *J. Amer. Chem. Soc.*, 1961, **83**, 3840 and 4216; G. W. Gokel, D. Marquarding, and I. K. Ugi, *J. Org. Chem.*, 1972, **37**, 3052; (b) T. D. Turbitt and W. E. Watts, *J. C.S. Perkin II*, 1974, 177.

<sup>14</sup> F. Bergmann and H. Japhe, *J. Amer. Chem. Soc.*, 1947, **69**, 1826.

<sup>15</sup> H. C. Brown, D. L. van der Jagt, P. von R. Schleyer, R. C. Fort, and W. E. Watts, *J. Amer. Chem. Soc.*, 1969, **91**, 6848.

powder, m.p. 174.5—176.5° (from light petroleum) (Found: C, 73.8; H, 7.8.  $C_{30}H_{38}FeO_2$  requires C, 74.1; H, 7.8%);  $\nu_{\max}$  ( $CCl_4$ ) 3 610—3 200  $cm^{-1}$  (OH);  $\tau$  ( $CDCl_3$ ) 5.6—6.05 (8 H, m, ferrocenyl), 6.58br (2 H, s, OH), 7.4 (2 H, q, bridgehead protons), and 7.8—9.4 (26 H, m, remaining protons).

2-endo-Methyl-exo-5,6-trimethylenenorbornan-2-ol (6a).—Concentrated hydrochloric acid (250 ml) was added dropwise over 2 h to a stirred solution of the alcohol (4a) (14.2 g, 85 mmol) in tetrahydrofuran (150 ml). A mildly exothermic reaction occurred. The mixture was stirred overnight and then poured into water (1 l). The organic product was extracted with ether in the usual way, giving a viscous, pale yellow liquid (16 g) which was immediately added to a slurry of calcium oxide (35 g) in water (300 ml). The mixture was stirred and heated under reflux for 24 h, then filtered. The filtrate was extracted thoroughly with ether and the extracts were combined with ethereal washings of the solid residue. The total extract was washed ( $H_2O$ ), dried ( $Na_2SO_4$ ), and evaporated, and the residue was dissolved in light petroleum and chromatographed ( $Al_2O_3$ ). Light petroleum eluted a viscous material (3.5 g) which was not investigated. Light petroleum-ether (4 : 1) eluted the alcohol (6a) (8.5 g, 60%), needles, m.p. 73—74° (from light petroleum) (lit.<sup>15</sup> 77.2—77.8°) (Found: C, 80.0; H, 11.2%;  $M$ , 166.1364. Calc. for  $C_{11}H_{18}O$ : C, 79.5; H, 10.8%;  $M$ , 166.1358);  $\nu_{\max}$  ( $CCl_4$ ) 3 608 and 3 500—3 350  $cm^{-1}$  (OH);  $\tau$  ( $CDCl_3$ ) 8.72 (3 H, s, Me) and 7.8—9.3 (15 H, m, remaining protons).

2-endo-Phenyl-exo-5,6-trimethylenenorbornan-2-ol (6b).—The reaction of the alcohol (4b) (9.7 g, 43 mmol) with hydrochloric acid followed by calcium oxide was carried out exactly as in the preceding experiment, and the product was chromatographed ( $Al_2O_3$ ). Light petroleum eluted the alkene (7b) (4.7 g, 50%), identical with the product described later. Light petroleum-ether (4 : 1) eluted unchanged (4b) (1.1 g, 12% recovery), followed by the alcohol (6b) (2.9 g, 30%), needles, m.p. 90—92° (from light petroleum) (lit.<sup>15</sup> 94.5—95.2°) (Found: C, 84.7; H, 8.6%;  $M$ , 228.1506. Calc. for  $C_{16}H_{20}O$ : C, 84.2; H, 8.8%;  $M$ , 228.1514);  $\nu_{\max}$  3 605  $cm^{-1}$  (OH);  $\tau$  ( $CDCl_3$ ) 2.4—2.8 (5 H, m, Ph) and 7.6—9.3 (15 H, m, remaining protons).

2-endo-Ferrocenyl-exo-5,6-trimethylenenorbornan-2-ol (6c).—Dry hydrogen chloride was bubbled through a stirred solution of the alcohol (4c) (7.7 g, 23 mmol) in light petroleum (150 ml) at 0 °C. After 1 h, the solution had become almost colourless and a dark red gum had been deposited on the sides of the flask. An excess of saturated aqueous sodium carbonate was then added, the two-layer system was stirred vigorously, and the organic layer was separated and combined with two ethereal extracts of the aqueous layer. The total extract was washed ( $H_2O$ ), dried ( $Na_2SO_4$ ), and evaporated, and the residue was dissolved in light petroleum and chromatographed ( $Al_2O_3$ ). Light petroleum eluted the alkene (7c) (5.2 g, 73%), identical with the product described later. Light petroleum-ether (3 : 2) eluted traces of the starting alcohol, followed by the alcohol (6c) (0.85 g, 11%), a yellow solid, m.p. 142.5—144.5° (from light petroleum) (Found: C, 71.0; H, 7.2.  $C_{20}H_{24}FeO$  requires C, 71.4; H, 7.1%);  $\nu_{\max}$  ( $CCl_4$ ) 3 565  $cm^{-1}$  (OH);  $\tau$  ( $CDCl_3$ ) 5.64—6.0 (9 H, m + s, ferrocenyl), 7.55 (1 H, s, OH), and 7.8—9.3 (14 H, m, remaining protons).

2-Phenyl-exo-5,6-trimethylenenorborn-2-ene (7b).—Phosphoryl chloride (16.2 g, 0.11 mol) was added dropwise to a

stirred solution of the alcohol (4b) (10 g, 0.044 mol) in dry pyridine (150 ml) at 0 °C. The mixture was stirred and allowed to come to room temperature during 2 h, and then was heated at 80 °C for 4 h. The solution was poured into water (1 000 ml) containing sodium chloride (10 g) and the mixture was extracted with ether. The extract was washed with dilute hydrochloric acid (four times), then water, dried ( $Na_2SO_4$ ), and evaporated. The residual gum was dissolved in light petroleum and chromatographed ( $Al_2O_3$ ). The same solvent eluted the alkene (7b) (7.5 g, 81%), a viscous liquid (Found: C, 91.2; H, 8.7%;  $M$ , 210.1407.  $C_{16}H_{18}$  requires C, 91.4; H, 8.6%;  $M$ , 210.1408);  $\nu_{\max}$  (film) 1 605  $cm^{-1}$  (C=C);  $\tau$  ( $CDCl_3$ ) 2.5—3.0 (5 H, m, Ph), 3.70 (1 H, d, vinyl), 7.1br and 7.4br (1 H and 1 H, s + d, bridgehead protons), and 7.7—9.3 (10 H, m, remaining protons).

2-Ferrocenyl-exo-5,6-trimethylenenorborn-2-ene (7c).—Dehydration of the alcohol (4c) was carried out as in the preceding experiment, giving the alkene (7c) (84%), a dark red liquid, crystallising at 0 °C (Found: C, 74.6; H, 7.1.  $C_{20}H_{22}Fe$  requires C, 75.5; H, 6.9%);  $\nu_{\max}$  (film) 1 610  $cm^{-1}$  (C=C);  $\tau$  ( $CDCl_3$ ) 4.01 (1 H, d, vinyl), 5.65—5.85 (4 H, m,  $C_5H_4$ ), 5.91 (5 H, m,  $C_5H_5$ ), and 7.3—9.2 (12 H, m, remaining protons). This compound is unstable in solution and at temperatures greater than 0 °C in the absence of solvent.

Dehydration of the Alcohol (4a).—Treatment of the alcohol (4a) in pyridine solution with phosphoryl chloride as in an earlier experiment gave a mixture of the alkenes (7a) and (8) (total yield 54%);  $\tau$  ( $CDCl_3$ ) 4.46br [s, vinyl proton of (7a)], 5.20 and 5.48 [ $2 \times$  d, vinyl protons of (8)], and 7.2—9.5 (remaining protons). Integration of the vinyl resonances gave the product ratio [(7a) : (8)] 1 : 4. Attempted separation of these alkenes by chromatography ( $SiO_2$  impregnated with  $AgNO_3$ ) was unsuccessful. Treatment of the mixture in turn with dry hydrogen chloride in chloroform solution and with potassium *t*-butoxide in *t*-butyl alcohol did not change the composition.

2-Methylene-exo-5,6-trimethylenenorbornane (8).—Methyltriphenylphosphonium iodide (49 g, 0.12 mol) was added to a solution of phenyl-lithium (0.12 mol) in dry ether (800 ml) and the suspension was stirred for 16 h. The ketone (3) (6.95 g, 0.05 mol) was then added and the mixture was stirred and heated under reflux for 24 h. The ether was then removed by distillation and was continuously replaced by dry tetrahydrofuran. The mixture was stirred and heated under reflux for 72 h, then filtered, and the filtrate was diluted with water (1 000 ml) and extracted thoroughly with ether. The extract was washed ( $H_2O$ ), dried ( $Na_2SO_4$ ), and evaporated, and the residue was dissolved in light petroleum and chromatographed ( $Al_2O_3$ ). The same solvent eluted the alkene (8) (4.4 g, 56%), a liquid, b.p. 92—94° at 20 mmHg (Found: C, 88.5; H, 11.5%;  $M$ , 149.1287.  $C_{11}H_{16}$  requires C, 89.2; H, 10.8%;  $M$ , 149.1285);  $\nu_{\max}$  1 669 and 874  $cm^{-1}$  (C=CH<sub>2</sub>);  $\tau$  ( $CDCl_3$ ) 5.20 and 5.48 (1 H and 1 H,  $2 \times$  d, vinyl), and 7.4—9.5 (14 H, m, remaining protons).

Reactions of Compounds (4a), (6a), and (8) with Formic Acid.—A solution of the substrate (ca. 0.04 mol) in 98% formic acid (25 ml) was stirred and heated at the temperature given for 2 h. The solvent was then removed under reduced pressure giving a mixture of the same products (mainly formates), in similar proportions (i.r., <sup>1</sup>H n.m.r., and t.l.c.), irrespective of starting material. This mixture was treated further as described below.

(a) *Reaction at 50 °C.* Aqueous chromic acid (8N; 32 ml) was added to a solution of the crude product mixture in acetone (200 ml). The mixture was stirred overnight, then diluted with water (2 l), and extracted thoroughly with ether. The extract was washed (H<sub>2</sub>O), dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated, and the residue was dissolved in light petroleum and chromatographed (Al<sub>2</sub>O<sub>3</sub>). Light petroleum-ether (10 : 1) eluted 1-methyl-endo-5,6-trimethylenenorbornan-2-one (9) (10%), an almost colourless liquid (Found: C, 81.1; H, 9.7%; *M*, 164.1177. C<sub>11</sub>H<sub>16</sub>O requires C, 80.5; H, 9.8%; *M*, 164.1201);  $\nu_{\max}$  (film) 1740 cm<sup>-1</sup> (CO);  $\tau$  (CDCl<sub>3</sub>) 7.1—7.6 (2 H, m, CH<sub>2</sub>CO), 7.7—8.9 (11 H, m, other protons), and 8.91 (3 H, s, Me). Light petroleum-ether (4 : 1) eluted the alcohols (4a) (35%) and (6a) (18%), identical with the compounds described earlier. Light petroleum-ether (1 : 1) eluted the diketone (10) (5%), identical with the product described later.

(b) *Reaction at 95 °C.* A solution of the crude product mixture in ethanol (200 ml) containing potassium hydroxide (25 g) was heated under reflux for 20 h, then diluted with water (2 000 ml), and extracted with ether. The extract was washed (H<sub>2</sub>O), dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated, and the residue was dissolved in light petroleum and chromatographed (Al<sub>2</sub>O<sub>3</sub>). The same solvent eluted a hydrocarbon (24%), a viscous liquid (Found: C, 89.0; H, 10.9%; *M*, 296.2496. Calc. for C<sub>22</sub>H<sub>32</sub>: C, 89.2; H, 10.8%; *M*, 296.2504);  $\tau$  (CDCl<sub>3</sub>) 4.5—5.0 (m, vinyl) and 7.5—9.2 (m, other protons). Light petroleum-ether eluted the alcohol (4a) (24%), identical with the compound described earlier, followed by 3-endo-methyl-exo-5,6-trimethylenenorbornan-2-exo-ol (13) (18%), needles, m.p. 64—66° (from light petroleum) (Found: C, 79.7; H, 11.1%; *M*, 166.1345. C<sub>11</sub>H<sub>18</sub>O requires C, 79.5; H, 10.8%; *M*, 166.1358);  $\nu_{\max}$  (CCl<sub>4</sub>) 3 620 and 3 500—3 300 cm<sup>-1</sup> (OH);  $\tau$  (CDCl<sub>3</sub>) 6.92 (1 H, d, CHOH), 8.3 (1 H, s, OH; D<sub>2</sub>O-exchangeable), 7.8—9.2 (13 H, m, other protons), and 9.05 (3 H, d, CHMe, *J* 7.2 Hz). Several other minor products were not identified.

*Reactions of Compounds (4b), (6b), and (7b) with Formic Acid.*—A solution of the substrate (*ca.* 0.02 mol) in 98% formic acid (25 ml) was stirred and heated at 70 °C for 2 h. The product was isolated by removal of the solvent under reduced pressure, and chromatographed (SiO<sub>2</sub>). Light petroleum eluted a mixture of two hydrocarbons (83%) which were separated by preparative t.l.c. (SiO<sub>2</sub>); the less polar hydrocarbon was obtained as plates, m.p. 226—228° (from light petroleum) (Found: C, 90.8; H, 8.9%; *M*, 420.2823. C<sub>32</sub>H<sub>36</sub> requires C, 91.4; H, 8.6%; *M*, 420.2817);  $\tau$  (CDCl<sub>3</sub>) 2.3—3.1 (10 H, m, Ph) and 7.4—9.6 (26 H, m, other protons); the more polar hydrocarbon was obtained as plates, m.p. 204—206° (from light petroleum) (Found: C, 91.2; H, 8.9%; *M*, 420.2792);  $\tau$  (CDCl<sub>3</sub>) 2.6—3.1 (10 H, m, Ph), and 7.0—9.5 (26 H, m, other protons).

From some of these reactions, but not reproducibly, there was also obtained, following preparative t.l.c., a colourless, viscous liquid containing two components which could not be completely separated (Found: *M*, 226.1343. C<sub>16</sub>H<sub>18</sub>O requires *M*, 226.1358);  $\nu_{\max}$  (film) 1 720 (CO) and 1 260 cm<sup>-1</sup> (epoxide?);  $\tau$  (CDCl<sub>3</sub>) 2.4—3.0 (m, Ph), 6.63 (s, CHOR), and 7.0—9.2 (m, other protons).

3-exo-Hydroxy-3-phenyl-exo-5,6-trimethylenenorbornan-2-exo-yl *m*-Chlorobenzoate (17a).—A solution of the alkene (7b) (7.5 g, 0.036 mol) and *m*-chloroperbenzoic acid (7.1 g, 0.041 mol) in dry chloroform (200 ml) was kept in the

dark for 6 days. The solvent was then evaporated off and the residue was chromatographed (SiO<sub>2</sub>). Light petroleum-ether (3 : 2) eluted the hydroxy-ester (17a) (10.3 g, 75%), needles, m.p. 138.5—140° (from methanol) (Found: C, 72.2; H, 6.0; Cl, 9.0. C<sub>23</sub>H<sub>23</sub>ClO<sub>3</sub> requires C, 72.3; H, 6.0; Cl, 9.2%);  $\nu_{\max}$  (CCl<sub>4</sub>) 3 605 (OH) and 1 726 cm<sup>-1</sup> (CO);  $\tau$  (CDCl<sub>3</sub>) 2.0—2.8 (9 H, m, aromatic), 4.61 (1 H, d, CH·O·CO), 7.58 (1 H, s, OH, D<sub>2</sub>O-exchangeable), and 7.7—9.3 (12 H, m, other protons).

2-Phenyl-exo-5,6-trimethylenenorbornane-2-exo,3-exo-diol (17b).—(a) A solution of osmium tetroxide (1 g, 4 mmol) in dry ether (45 ml) was added to a solution of the alkene (7b) (0.91 g, 4 mmol) in dry ether (100 ml). A black precipitate was formed immediately. The mixture was kept in the dark for 3 days and then evaporated. The residue was suspended in ethanol (150 ml) containing sodium disulphite (7 g). The mixture was heated under reflux for 3 h, filtered, diluted with water (150 ml), and extracted thoroughly with chloroform. The extract was washed (H<sub>2</sub>O), dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated, and the residue was chromatographed (Al<sub>2</sub>O<sub>3</sub>). Light petroleum eluted unchanged alkene (0.06 g, 7% recovery). Light petroleum-ether (1 : 1) eluted the diol (17b) (0.70 g, 62%), a solid, m.p. 83.5—84.5° (from light petroleum) (Found: C, 78.9; H, 8.6%; *M*, 244.1456. C<sub>16</sub>H<sub>20</sub>O<sub>2</sub> requires C, 78.7; H, 8.2%; *M*, 244.1463);  $\nu_{\max}$  (CCl<sub>4</sub>) 3 600 and 3 560—3 100 cm<sup>-1</sup> (OH);  $\tau$  (CDCl<sub>3</sub>) 2.4—2.9 (5 H, m, Ph), 6.00 (1 H, d, CHOH), 6.55 (1 H, d, OH), 6.93 (1 H, s, OH), and 7.7—9.2 (12 H, m, other protons).

(b) A solution of the hydroxy-ester (17a) (9.9 g, 0.026 mol) in methanol (150 ml) containing potassium hydroxide (2.8 g) was heated under reflux for 16 h, then diluted with water (1 l), and extracted with ether. The extract was washed (dilute aq. NaOH, then H<sub>2</sub>O), dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated, and the residue was chromatographed (Al<sub>2</sub>O<sub>3</sub>), giving the diol (17b) (4.3 g, 67%), identical with the product described in (a).

*Attempted Pinacol Rearrangement of the Diol (17b).*—Concentrated sulphuric acid (12.5 ml) was added dropwise over 10 min to a stirred, ice-cooled solution of the diol (17b) (1.13 g) in dioxan (15 ml). The mixture was stirred for 10 min and then poured into water (500 ml) and extracted with ether. T.l.c. showed the presence of a complex mixture of products which was not investigated further.

*Reactions of Compounds (4c), (6c), and (7c) with Formic Acid.*—Dissolution of the substrate (*ca.* 5 mmol) in 98% formic acid (60 ml) gave a dark red solution containing the cation (2c). The solution was stirred at room temperature for 16 h, then diluted with water (250 ml), and extracted with ether. The extract was washed (aq. Na<sub>2</sub>CO<sub>3</sub>, then H<sub>2</sub>O), dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated, and the residue was chromatographed (Al<sub>2</sub>O<sub>3</sub>). Irrespective of starting material, there was obtained, in order of elution, the alkene (7c) (55%), the alcohol (4c) (34%), and the alcohol (6c) (7%), identical with the compounds described earlier.

*Generation of Stereoisomeric Cations (18A and B).*—The alcohol (4c) was dissolved in trifluoroacetic acid and the <sup>1</sup>H n.m.r. spectrum of the resulting solution of the cation (18A) was immediately recorded:  $\tau$  3.5—3.8 (2 H, m) and 4.95—5.05 (2 H, m) (C<sub>5</sub>H<sub>4</sub>), 5.08 (5 H, s, C<sub>5</sub>H<sub>5</sub>), and 7.0—9.0 (14 H, m, other protons). This spectrum was unchanged with time.

Similarly, the alcohol (6c) afforded the cation (18B):  $\tau$  (CF<sub>3</sub>·CO<sub>2</sub>H) 3.45—3.55 (1 H, m), 3.6—3.75 (1 H, m), and

4.75—4.9 (2 H, m) ( $C_5H_4$ ), 5.02 (5 H, m,  $C_5H_5$ ), and 7.0—9.0 (14 H, m, other protons). This spectrum changed with time, giving finally a spectrum identical with that of the cation (18A). The growth and decay of the well-resolved ( $C_5H_5$ ) singlet resonances of the stereoisomers were particularly easy to monitor.

Dissolution of the alkene (7c) in trifluoroacetic acid gave

a solution the  $^1H$  n.m.r. spectrum of which was identical with that of (18A).

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