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ALICYCLIC STUDIES—X*

THE BICYCLO-(5:4:0)-2-UNDECANONES

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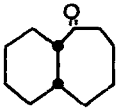
Abstract—The stereochemistry of the bicyclo-(5:4:0)-2-undecanones is discussed. The cis-*ketone* is obtained by catalytic reduction of benzosuberone and is converted into the trans-*ketone* by treatment with sodium methoxide. Dehydrogenation experiments of both isomers are described.

IN the α-hydrindanone system the *cis* isomer is known to be conformationally more stable than the *trans* compound.[2] In the α-decalone system the reverse situation obtains.[3] It was of interest to determine the relative stabilities of the next higher homologues, the bicyclo-(5:4:0)-2-undecanones (hexahydrobenzosuberones).

The aromatic ring of benzosuberone cannot be hydrogenated in the presence of Adams catalyst without concomitant reduction of the carbonyl group and hydrogenolysis of the resulting benzyl-type alcohol.[4] It was found that a quantitative yield of *cis*-bicyclo-(5:4:0)-2-undecanol can be obtained by employing ruthenium oxide as the hydrogenation catalyst. This alcohol clearly does not suffer hydrogenolysis in the presence of ruthenium and can be oxidised in high yield by means of chromic anhydride in acetic acid to the cis-*ketone*(I). This ketone does not isomerise under the conditions employed for formation of its oxime, semicarbazone, or 2:4-dinitrophenylhydrazone, but it can be isomerised to the trans-*ketone*(II) by treatment with sodium methoxide. The trans-*ketone* affords a different set of derivatives from that given by its *cis* isomer.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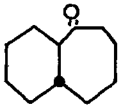
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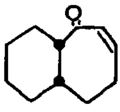
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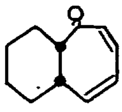
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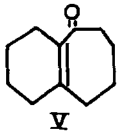
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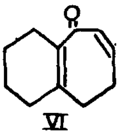
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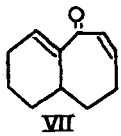
VII

It is important to note that the same alcohol results on catalytic reduction of benzosuberone and benzosuberol, thus ruling out any possibility of a mechanism of 1:4-reduction in the case of the ketone.

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[*] Part IX *J. Chem. Soc.* 1301 (1957).

[1] Presented at XIVth Congress of the International Union of Pure and Applied Chemistry, Zurich, July 1955. *Abstr. of Congress*, p. 49.

[2] E. L. Eliel and C. Pillar *J. Amer. Chem. Soc.* **77**, 3600, who also gives leading references (footnote 3) (1955).

[3] W. Hückel and E. Brinkmann *Annalen* **441**, 21 (1925).

[4] Pl. A. Plattner *Helv. Chim. Acta* **27**, 801 (1944).

Dehydrogenation experiments were carried out both with the *cis*- and *trans*-bicyclo-(5:4:0)-2-undecanones. Thus, when the cis-*ketone* was treated with 1 mole of selenium dioxide, a monoenone, formulated as (III), was obtained. When the latter was treated with 1 mole of *N*-bromosuccinimide followed by dehydrobromination or when the cis-*ketone* was treated with two moles of selenium dioxide, the same product, a dienone, formulated as (IV), was obtained. Further treatment of the dienone with *N*-bromosuccinimide had no effect.

Clearly the molecular shape of the cis-*ketone* does not permit attack of any of the above reagents at the ring junction; even after two double bonds had been introduced, the driving force of potential formation of a tropone derivative is not sufficient to counteract this geometrical influence.

In the case of the trans-*ketone*, however, excess of selenium dioxide (2 moles) introduces only one double bond, presumably at the junction of both rings. Here no similar hindrance exists, and the first step is probably hydroxylation at the tertiary ring junction α to the carbonyl group and ready *trans* elimination of water is possible with the formation of (V). Treatment of this product with *N*-bromosuccinimide followed by dehydrobromination leads to a cross-conjugated dienone (VI) or (VII). (See experimental section for spectroscopic data upon which these formulations are based.)

EXPERIMENTAL*

cis-*Bicyclo*-(5:4:0)-2-*undecanol*

Benzosuberone[5] (10 g) in ethyl acetate (100 ml) was hydrogenated in the presence of ruthenium oxide (0·7 g) at an initial pressure of 1000 lb/sq. in. and 80°C. Hydrogen uptake (4 moles) stopped after 2·5 hr. After removal of the catalyst by filtration and the solvent by distillation, the *alcohol* was distilled, b.p. 112–113°/3 mm n_D^{25} 1·5078. Infra-red absorption (CCl_4): 3610 cm^{-1} (OH). Ultra-violet absorption: none (Found: C, 78·2; H, 12·0. $C_{11}H_{20}O$ requires C, 78·5; H, 12·0%).

The p-*nitrobenzoate* formed colourless crystals, m.p. 122–123° (from methanol-chloroform) (Found: C, 68·2; H, 7·9; N, 4·4. $C_{18}H_{23}NO_4$ requires C, 68·1; H, 7·3; N, 4·4%).

Careful fractionation of 50 g of the alcohol at 20 mm using a 25-plate column gave several preliminary fractions which gave a strong coloration with tetranitromethane (1 g), which evidently formed by partial dehydration of the alcohol during the distillation. The distillate was then divided into twelve fractions which boiled in the range 147–152°/20 mm and had n_D^{25} in the range 1·5076–1·5082. *p*-Nitrobenzoates of the first and last of these fractions both had m.p. 122–123° (from methanol-chloroform) and showed no depression in melting-point on admixture. No separation could therefore be accomplished between the possible axial and equatorial alcohols, and it appears that only the α-ol was formed in the hydrogenation.

cis-*Bicyclo*-(5:4:0)-2-*undecanone*

cis-Bicyclo-(5:4:0)-2-undecanol (100 g) was dissolved in acetic acid (A.R.; 200 ml), cooled in an ice-bath and a solution of chromic acid (A.R.; 44 g; 1·1 mole) in water (20 ml), and acetic acid (100 ml) was added over a period of 1 hr with cooling and stirring. The mixture was allowed to stand overnight at room temperature, and

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* Melting- and boiling-points are uncorrected.

[5] R. C. Gilmore jr. and W. J. Horton *J. Amer. Chem. Soc.* 73, 1413 (1951).

methanol (5 ml) was added. After careful neutralisation with solid sodium bicarbonate, water was added and the solution was extracted with ether. After working up in the usual way, distillation afforded a forerun, b.p. below 78°/1 mm (3 g); and the ketone, b.p. 78–82°/1 mm (79 g), and a further quantity of the ketone, b.p. 82–90°/1 mm (17 g). The middle fraction was cooled in an alcohol–dry-ice bath, and two-thirds of the solidified product was allowed to melt and the liquid portion was decanted. The residue was allowed to melt and was refrozen. When two-thirds had again melted, the liquid was decanted and the residue which is pure cis-*ketone* had n_D^{25} 1·4930; d_4^{25} 0·9982 (Found: C, 79·9; H, 11·3. $C_{11}H_{18}O$ requires C, 79·5; H, 10·9%).

The orange 2:4-*dinitrophenylhydrazone* was prepared at room temperature and was recrystallised six times, from cold methanol-chloroform, m.p. 145–146° (Found: C, 59·3; H, 6·5; N, 16·3. $C_{17}H_{22}N_4O_4$ requires C, 58·9; H, 6·4; N, 16·2%).

The *oxime* formed colourless needles, m.p. 100–101° (from methanol) (Found: C, 72·8; H, 10·8; N, 7·2. $C_{11}H_{19}NO$ requires C, 72·9; H, 10·6; N, 7·7%).

The *semicarbazone* formed colourless crystals, m.p. 201–202° (from ethanol-chloroform) (Found: C, 65·0; H, 9·8; N, 18·6. $C_{12}H_{21}N_3O$ requires C, 64·5; H, 9·5; N, 18·8%).

trans-*Bicyclo*-(5:4:0)-2-*undecanone*

The isomerisation was carried out by dissolving cis-*ketone* (30 g) in a solution of methanol (100 ml) containing sodium methoxide (0·5 g). The solution was heated under reflux for 30 min, concentrated *in vacuo* to a volume of 50 ml, and poured into water. The mixture was neutralised with dilute hydrochloric acid and extracted with ether. After working up in the usual way, distillation afforded the trans-*ketone*, b.p. 72–74°/0·5 mm (27 g).

The product was recrystallised twice by freezing as described for the *cis*-isomer, and had n_D^{25} 1·4906, d_4^{25} 0·9856 (Found: C, 79·5; H, 11·3. $C_{11}H_{18}O$ requires C, 79·5; H, 10·9%).

The orange 2:4-*dinitrophenylhydrazone*, m.p. 173–174° (from methanol-chloroform) (Found: C, 58·8; H, 6·8; N, 16·1. $C_{17}H_{22}N_4O_4$ requires C, 58·9; H, 6·4; N, 16·2%).

The *oxime* formed colourless needles, m.p. 128–129° (from methanol) (Found: C, 73·0; H, 10·3; N, 7·7. $C_{11}H_{19}NO$ requires C, 72·9; H, 10·6; N, 7·7%).

The *semicarbazone* formed colourless crystals, m.p. 213–214° (from ethanol-chloroform) (Found: C, 65·0; H, 9·6; N, 19·1. $C_{12}H_{21}N_3O$ requires C, 64·5; H, 9·5; N, 18·8%).

Refluxing the trans-*ketone* in methanol containing a trace of sodium methoxide for longer periods of time (2-3 hr) has no effect and no dimerisation takes place during this period.

Benzylidene derivative of the trans-*ketone*

trans-*ketone* (2 g) and freshly distilled benzaldehyde were dissolved in methanol (20 ml), sodium methoxide (0·5 g) added, and the mixture was allowed to stand for 2 days in a stoppered flask at room temperature. Water was added until the solution just assumed turbidity, and the mixture was left standing overnight. The precipitate was removed by filtration and was recrystallised four times from methanol, giving long needles, m.p. 133–134° (Found: C, 79·6; H, 8·9. $C_{18}H_{22}O{\cdot}H_2O$ requires C, 79·4; H, 8·9%).

Sodium-alcohol reduction of trans-*ketone*

The trans-*ketone* (10 g) was dissolved in *n*-propanol (200 ml), the solution was heated to reflux, and sodium (20 g) was added in small pieces over a period of 2 hr. The solution was refluxed for an additional hour to ensure complete dissolution of the sodium. After working up in the usual way, distillation and redistillation afforded the trans-*bicyclo*-(5:4:0)-*undecan-2β-ol* (equatorial isomer), b.p. 113–114°/3 mm n_D^{25} 1·5002 (Found: C, 78·2; H, 11·6. $C_{11}H_{20}O$ requires C, 78·5; H, 12·0%).

The p-*nitrobenzoate* formed colourless crystals, m.p. 89–90° (from chloroform-methanol) (Found: C, 68·7; H, 8·1; N, 4·7. $C_{18}H_{23}NO_4$ requires C, 68·1; H, 7·3; N, 4·4%).

Hydrogenation with platinum oxide

The trans-*ketone* was hydrogenated in ethanol solution in the presence of Adams catalyst at room temperature and atmospheric pressure. After completion of hydrogen uptake (2 hr), the catalyst and solvent were removed and the *α-alcohol* was distilled in high vacuum, b.p. 83–84°/0·4 mm, n_D^{25} 1·4937. It was characterized as the p-*nitrobenzoate* which formed colourless needles, m.p. 87–87·5° (from chloroform-methanol). On admixture with the *p*-nitrobenzoate of the alcohol resulting from sodium-alcohol reduction of the trans-*ketone*, m.p. 89–90° (see above), the melting-point was depressed to 69–71°. The alcohol obtained by catalytic reduction is presumably the α-(axial) isomer.

Clemmensen-Martin reduction of trans-*ketone*

In a 1-litre three-necked flask fitted with a stirrer, gas-inlet tube, and reflux condenser, were placed freshly amalgamated granulated zinc (50 g), water (50 ml), and concentrated hydrochloric acid (100 ml). The mixture was heated to boiling with stirring and a solution of the trans-*ketone* (15 g) in toluene (50 ml) was slowly added. After 2, 6, 8, 12, 15, 18, and 20 hr the stirred boiling mixture was saturated with hydrogen chloride. All the zinc had dissolved, but the mixture on testing with 2:4-dinitrophenylhydrazine still contained ketone. More amalgamated zinc (10 g) was added, and the solution was again saturated with hydrogen chloride. No ketone remained at the end of 30 hr of heating.

The toluene layer was separated. The aqueous layer was almost neutralised with sodium carbonate solution, care being taken not to precipitate zinc hydroxide. The solution was extracted with ether, the ether and toluene solutions were combined, washed with dilute hydrochloric acid and with water, and dried over anhydrous sodium sulphate. The solvents were removed by distillation and the residue was distilled over potassium. The hydrocarbon had b.p. 130–140°/40 mm (13 g).

In order to remove any unsaturated material, the product was dissolved in acetic acid (A.R.; 50 ml), and chromic acid (A.R.; 0·5 g) in acetic acid (90%; 10 ml) was added. The solution was warmed on the steam bath for 2 hr and was worked up and separated into acidic and neutral fractions. The neutral fraction distilled at 105–115°/24 mm and was then carefully fractionated: forerun, b.p. 105–108°/24 mm (1 g); main fraction of trans-*bicyclo*-(5:4:0)-*undecane*, b.p. 108–109°/24 mm (9 g); third fraction, b.p. 109–114°/24 mm (2 g). The main fraction had n_D^{25} 1·4816; n_D^{20} 1·4836; d_4^{20} 0·9140 (Found: C, 86·9; H, 13·4. $C_{18}H_{20}$ requires C, 86·8; H, 13·2%). Plattner[4] reported for the *cis*-hydrocarbon d_4^{20} 0·9014; b.p. 88·5–89°/11 mm; n_D^{20} 1·4845.

Hydrogenation of benzosuberol with ruthenium dioxide

Crystalline benzosuberol (5 g) was dissolved in ethyl acetate (40 ml) and hydrogenated in the presence of ruthenium dioxide (0·3 g) at an initial pressure of 930 lb/sq. in. at 80°. After 3 hr hydrogen uptake was complete and corresponded to 3 moles of hydrogen. After filtration of the catalyst and removal of the solvent, the alcohol was characterised as the *p*-nitrobenzoate, m.p. and mixed m.p. with the corresponding derivative obtained by catalytic reduction of benzosuberone (see above), 123–124°.

Oxidation of benzosuberol with pyridine-chromic acid complex

Benzosuberol (300 mg) in pyridine (3 ml) was added to chromic anhydride (300 mg) in pyridine (10 ml), and the mixture was allowed to stand overnight. After working up in the usual manner, the benzosuberone was characterized as its orange 2:4-*dinitrophenylhydrazone*, m.p. 213–214° (from chloroform-methanol), undepressed on admixture with an authentic sample. Ultra-violet absorption (chloroform): λ_{max} 3750 Å; ε 28,700 (Found: C, 59·8; H, 4·9; N, 16·8. $C_{17}H_{16}N_4O_4$ requires C, 60·0; H, 4·7; N, 16·5%).

Benzosuberone dioxolane

The substance was prepared in 85% yield by azeotropic distillation of a mixture of benzosuberone, ethylene glycol, and toluene in the presence of a trace of *p*-toluenesulphonic acid and working up in the usual way. It had m.p. 60–62° (from benzene) (Found: C, 76·5; H, 7·9. $C_{13}H_{16}O_2$ requires C, 76·4; H, 7·9%).

Dehydrogenation experiments with trans-*bicyclo*-(5:4:0)-2-*undecanol*

(a) A mixture of the trans-*ketone* (10 g) acetic anhydride (80 ml) and hydrated selenium dioxide (20 g) was heated under reflux for 3 hr. After the usual workup the *α,β-ethylenic ketone*(V), b.p. 128–132°/20 mm was obtained and characterised as the red 2:4-*dinitrophenylhydrazone*, flat needles, m.p. 170–171° (from ethyl acetate-ethanol). Ultra-violet absorption (chloroform): λ_{max} 3690 Å; ε_{max} 24,100 (Found: N, 16·4. $C_{17}H_{18}O_4N_4$ requires N, 16·4%). (b) The above product (3·2 g) was refluxed for 2 hr with *N*-bromosuccinimide (3 g; 1 mole) in dry carbon tetrachloride (25 ml). After the usual workup the residue was treated with lutidine to effect dehydrobromination and the *doubly-unsaturated ketone*(VI) or (VII) was distilled, b.p. 160–162°/30 mm n_D^{25} 1·5083. Ultra-violet absorption (chloroform): λ_{max} 2380 Å; ε_{max} 3320. Infra-red absorption (chloroform): 1692 cm^{-1}; 1615 cm^{-1}. It was characterized as the dark red 2:4-*dinitrophenylhydrazone*, needles, m.p. 191–192° (from chloroform-ethanol). Ultra-violet absorption (chloroform): λ_{max} 3760 Å; ε_{max} 27,400 (Found: N, 16·3. $C_{17}H_{16}O_4N_4$ requires N, 16·4%). The *semicarbazone* formed colourless crystals, m.p. 205–206° (from methanol). Ultra-violet absorption (EtOH): λ_{max} 2310 Å; ε_{max} 10,500.

Dehydrogenation experiments with cis-*bicyclo*-(5:4:0)-2-*undecanol*

(a) The cis-*ketone* was treated with 1 mole selenium dioxide, as described above for the trans-*ketone*. The *α,β-ethylenic ketone*(III) had b.p. 136–139°/20 mm, n_D^{25} 1·4916. Ultra-violet absorption (EtOH): λ_{max} 2410 Å; ε_{max} 9100. Infra-red absorption (CCl_4): 1697 cm^{-1}; 1620 cm^{-1}.

The *semicarbazone* formed colourless crystals, m.p. 190–191° (from methanol). Ultra-violet absorption: $\lambda_{\max}$ 2300 Å; $\varepsilon_{\max}$ 11,150 (Found: C, 65·0; H, 9·4; N, 19·0. $C_{12}H_{19}ON_3$ requires C, 65·1; H, 8·7; N, 19·0%).

The 2:4-*dinitrophenylhydrazone* formed red plates, m.p. 177–178° (from chloroform-methanol). Ultra-violet absorption (chloroform): $\lambda_{\max}$ 3715 Å; $\varepsilon_{\max}$ 26,700 (Found: N, 16·3. $C_{17}H_{18}O_4N_4$ requires N, 16·4%). (b) The *cis*-ketone was treated with 2 moles selenium dioxide, as described above. The doubly-unsaturated ketone(IV) was characterised as the *semicarbazone*, colourless crystals, m.p. 224–225° (from methanol), and the red 2:4-*dinitrophenylhydrazone*, m.p. 201–202°. Ultra-violet absorption (chloroform): $\lambda_{\max}$ 3810 Å; $\varepsilon_{\max}$ 22,000 (Found: C, 59·6; H, 5·8; N, 16·6. $C_{17}H_{16}O_4N_4$ requires C, 59·6; H, 5·3; N, 16·4%). The same ketone was obtained by treatment of the corresponding monoenone with 1 mole of *N*-bromosuccinimide. (c) Treatment of the dienone with *N*-bromosuccinimide followed by the usual workup yielded the unchanged dienone.