243. *Alicyclic Studies. Part IV.** 11-*Oxo*cyclo*hepta*[a]*naphthalene.*

By Dov Elad and David Ginsburg.

The synthesis of 11-oxo*cyclo*hepta[*a*]naphthalene (II) from an alicyclic intermediate is described.

The synthesis [1] of the *trans*-compound (I) made available a starting material for the preparation of 11-oxo*cyclo*hepta[*a*]naphthalene (II). There have been conflicting reports as to the ability of dibenzo[*a, e*]*cyclo*heptatrienone (III) to form ketonic derivatives [2,3,4] but it seems clear that it forms a 2 : 4-dinitrophenylhydrazone in contradistinction to the behaviour of tropone [5] itself, owing to the absence of coplanarity in the tricyclic compound (III). Examination of models indicates that the analogue (II) is coplanar and thus might be expected to exhibit behaviour more analogous to that of tropone.

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* Part III, *J.*, 1954, 2955.

[1] Ginsburg and Pappo, *J. Amer. Chem. Soc.*, 1953, **75**, 1094.

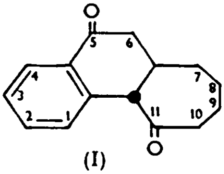
[2] Bergmann, Fischer, Ginsburg, Hirshberg, Lavie, Mayot, Pullman, and Pullman, *Bull. Soc. chim. France*, 1951, **18**, 684.

[3] Buchanan, *Chem. and Ind.*, 1952, 855.

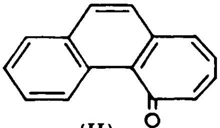
[4] Bergmann and Ginsburg, *ibid.*, 1954, 45.

[5] Doering and Detert, *J. Amer. Chem. Soc.*, 1951, **73**, 876.

Catalytic reduction of the diketone (I) removed the carbonyl group conjugated to the aromatic nuceleus and stepwise bromination and dehydrobromination afforded the naphthalenic ketone (IV). Although treatment of this with *n*-pentyl nitrite and sodium ethoxide afforded the α-hydroxyimino-ketone which in turn was converted through acid hydrolysis into the (enolised) α-diketone (V), all attempts to introduce an additional double bond in order to form the corresponding naphthotropolone failed.



(I)



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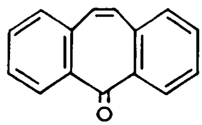
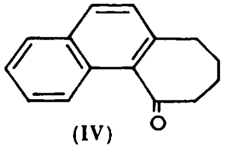
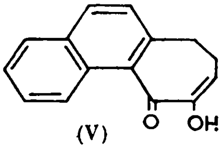


(III)



(IV)



(V)

However, stepwise bromination and dehydrobromination of the tetrahydro-ketone (IV) afforded the desired compound (II). No ketonic derivative could be prepared but a very unstable and hygroscopic picrate was formed which could not be characterised in pure form.

EXPERIMENTAL

Infrared and ultraviolet spectra were measured in $CHCl_3$ and MeOH, respectively.

6 : 6a : 7 : 8 : 9 : 10 : 11 : 11a-*Octahydro*-11-*oxo*-5H-cyclo*hepta*[a]*naphthalene.*—The diketone (I) (12 g.) was hydrogenated in acetic acid (150 ml.) in the presence of 10% palladised charcoal (1·2 g.) at 60—70° at an initial hydrogen pressure of 60 lbs./sq. in. Hydrogen uptake ceased after 3 hr. The catalyst was filtered off, the solvent was removed by distillation, and the residue was distilled in a high vacuum. The first fraction (9·5 g.) consisted of the desired *ketone*, b. p. 160—162°/1·5 mm. The higher-boiling fraction (1·5 g.) was recovered diketone, b. p. 177—180°/0·7 mm. The product crystallised very slowly and had m. p. 80—81·5° (from ethanol) (Found: C, 83·7; H, 8·8. $C_{15}H_{18}O$ requires C, 84·1; H, 8·5%). Infrared absorption: 1703 cm.$^{-1}$ (C=O). Ultraviolet absorption: 2660, 2810—2850 Å (log ε 2·79, 2·30).

The *oxime* formed colourless needles, m. p. 145—147° (from aqueous ethanol) (Found: C, 78·5; H, 8·3; N, 6·2. $C_{15}H_{19}ON$ requires C, 78·6; H, 8·35; N, 6·1%). Ultraviolet absorption: 2660 Å (log ε 3·57).

6 : 7 : 8 : 9 : 10 : 11-*Hexahydro*-11-*oxo*cyclo*hepta*[a]*naphthalene.*—A mixture of the above ketone (710 mg., 0·003 mole), *N*-bromosuccinimide (650 mg., 0·0033 mole), carbon tetrachloride (15 ml.), and several crystals of dibenzoyl peroxide was heated under reflux, soon becoming pale orange. The colour suddenly disappeared after a few minutes. After 30 min. of boiling all of the heavy brominating agent had been converted into succinimide which floated on the surface. Some hydrogen bromide evolution was observed. The succinimide was removed by filtration, and the solvent under reduced pressure. Attempts to crystallise the residue failed. 2 : 6-Lutidine (15 ml.) was added to the residue and the mixture was refluxed for 2 hr. After the usual working up [6] the αβ-unsaturated ketone was obtained as an oil (690 mg.), b. p. 161—163°/0·5 mm. Infrared absorption: 1685 cm.$^{-1}$ (C=O). This was characterised as the *oxime*, needles, m. p. 143—145° (from aqueous methanol) (admixture with the oxime of the starting material gave a depression to 120—126°) (Found: C, 78·9; H, 7·7; N, 6·4. $C_{15}H_{17}ON$ requires C, 79·3; H, 7·5; N, 6·2%). Ultraviolet absorption: 2240, 2670 Å (log ε 3·26, 2·39).

When larger quantities (5—10 g.) of ketone were brominated, the reaction was exothermic and was complete in 10—15 min.

6 : 7 : 8 : 9-*Tetrahydro*-11-*oxo*cyclo*hepta*[a]*naphthalene.*—The αβ-ethylenic ketone (3·55 g.)

[6] Elad and Ginsburg, *J.*, 1954, 471.

after bromination with *N*-bromosuccinimide as above (1·5 hr. to complete reaction) and dehydrobromination with 2 : 6-lutidine gave the naphthalenic *ketone* (IV) (2·84 g.), b. p. 178—182°/1·1 mm. Infrared absorption : 1675 cm.$^{-1}$ (C=O). The *oxime* formed needles, m. p. 158—160° (from aqueous ethanol) (Found : C, 79·85; H, 6·7; N, 6·2. $C_{15}H_{15}ON$ requires C, 80·0; H, 6·7; N, 6·2%). Ultraviolet absorption : 2270, 2870 Å (log ε 4·73, 3·71).

6 : 7 : 8 : 9-*Tetrahydro*-10-*hydroxyimino*-11-*oxo*cyclo*hepta*[a]*naphthalene*.—To a solution of sodium ethoxide [from 115 mg. (0·005 mole) of sodium and 3 ml. of ethanol] was added a solution of the ketone (IV) (1·05 g., 0·005 mole) in ethanol (5 ml.). *n*-Pentyl nitrite (0·69 ml.) was added to the ice-cold solution and the homogeneous solution was left at 0° for 24 hr. Ether, water, and acetic acid (1 ml.) were added and the aqueous phase was extracted with several portions of ether. The combined ether solutions were extracted with Claisen's alkali. Acidification of the latter with acetic acid precipitated an oil which crystallised. The *hydroxyimino-ketone* (0·8 g.) was triturated with methanol and had m. p. 169—171° (decomp.). Recrystallisation from ethanol yielded a sample, m. p. 183—185° (decomp.) (Found : C, 75·6; H, 5·3; N, 5·8. $C_{15}H_{13}O_2N$ requires C, 75·3; H, 5·5; N, 5·85%). A dioxan solution of this substance gives a green colour with alcoholic ferric chloride.

α-*Phenyltropolone*.—A mixture of 2-phenyl*cyclo*hept-2-enone [1] (0·93 g., 0·005 mole), dioxan (40 ml.), and selenium dioxide (0·62 g., 0·0055 mole) was refluxed for 4·5 hr. The precipitated selenium was filtered off and the dioxan was removed under reduced pressure. The residue was dissolved in ether and was washed many times with dilute silver nitrate solution and then with water. Evaporation of the ether gave an oil (850 mg.) which gave a green colour with alcoholic ferric chloride. This residue was refluxed in 1 : 2 : 4-trichlorobenzene (15 ml.) with 10% palladised charcoal (1·5 g.) for 5 hr. under nitrogen. After cooling and dilution with benzene, the solution was washed with sodium carbonate solution and with 2N-sodium hydroxide. The emulsion was destroyed with ether. Acidification of the alkaline extracts, and chloroform extraction, followed by removal of the solvent, gave a residue (60 mg.). Treatment with boiling hexane gave a solution which on concentration deposited α-phenyltropolone, m. p. 116—116·5° (from hexane). Doering and Mayer [7] report m. p. 116—116·5° and the infrared and ultraviolet absorption spectra which they report are superimposable on those of our product.

8 : 9-*Dihydro*-10-*hydroxy*-11-*oxo*cyclo*hepta*[a]*naphthalene*.—To a solution of the hydroxyiminoketone (0·5 g.) and sodium nitrite (1·2 g.) in 1 : 1 aqueous methanol (200 ml.) was added with stirring and cooling concentrated sulphuric acid (1·2 ml.). The solution was kept at 35—40° for 36 hr. with occasional stirring to dissolve the solid. Finally, a yellow homogeneous solution was obtained. The pH was adjusted to 6 by means of aqueous sodium carbonate. The mixture was concentrated under reduced pressure to about one-half of its original volume (bath-temp. 60°). The oil which was precipitated was taken up in ether, and the extract was washed with water. The residue obtained on evaporation of the ether (450 mg.) gave a dark brown colour with alcoholic ferric chloride and contained no nitrogen. Infrared absorption : 1684 cm.$^{-1}$ (C=O). It was characterised as the red 2 : 4-*dinitrophenylhydrazone*, m. p. 259·5—260·5° (from chloroform–ethanol) (Found : C, 62·75; H, 3·6; N, 13·9. $C_{21}H_{16}O_5N_4$ requires C, 62·4; H, 4·0; N, 13·9%). Attempts to dehydrogenate this substance to the tropolone, including treatment as described above for the preparation of α-phenyltropolone, failed.

Bromination Experiments towards Synthesis of 11-*Oxo*cyclo*hepta*[a]*naphthalene*.—(*a*) To a solution of the ketone (IV) (2·1 g., 0·01 mole) in carbon tetrachloride (10 ml.) was added at room temperature bromine (1·1 ml., 0·02 mole) in carbon tetrachloride (4 ml.). The solution was kept for 1 hr. with occasional shaking. The colour disappeared after the solution had been heated on the steam-bath for an additional 10 min. Removal of the solvent under reduced pressure gave a solid residue, whence trituration with hexane yielded the crystalline 6 : 6-*dibromo-compound* [8] (2 g.), m. p. 144—146° (from hexane). Concentration of the hexane solution gave further crops (0·4 g.) (Found : Br, 43·8. $C_{15}H_{12}OBr_2$ requires Br, 43·5%). Infrared absorption : 1707 cm.$^{-1}$ (C=O).

(*b*) A mixture of the dibromo-ketone (1 g.), tributylamine (8 ml.), and tetralin (25 ml.) was refluxed for 12 hr.[8] The precipitate of tributylamine hydrobromide was filtered off and the solvents were removed under reduced pressure. The oily residue was dissolved in ether and washed with dilute hydrochloric acid and with water. Evaporation yielded the 6-*bromo*-$\Delta^{6(7)}$-*ketone* as an oil (Found : Br, 27·0. $C_{15}H_{11}OBr$ requires C, 27·5%).

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[7] Doering and Mayer, *J. Amer. Chem. Soc.*, 1953, **75**, 2387.

[8] Cf. Lyle and Covery, *J. Amer. Chem. Soc.*, 1953, **75**, 4973.

(*c*) To a boiling solution of the ketone (IV) (1·05 g., 0·005 mole) in carbon tetrachloride (10 ml.) was added bromine (0·27 ml., 0·005 mole) in carbon tetrachloride (4 ml.). The bromine colour disappeared at once. Refluxing was continued for 1 hr. Removal of the solvent afforded an oil which was dissolved in ether and washed with aqueous sodium carbonate and with water. Removal of the ether gave the 6-*bromo-ketone* as an oil (Found: Br, 27·0. $C_{15}H_{13}OBr$ requires Br, 27·3%).

(*d*) A mixture of the 6-bromo-ketone (1·45 g., 0·02 mole), *N*-bromosuccinimide (0·84 g., 0·02 mole), carbon tetrachloride (15 ml.), and several crystals of dibenzoyl peroxide was refluxed for 2·5 hr. Some evolution of hydrogen bromide was observed. After removal of the succinimide and the solvent, the oily residue could not be induced to crystallise. Seeding with the crystalline 6 : 6-dibromo-ketone did not induce crystallisation. The residue is therefore believed to be partially dehydrobrominated 6 : 9-dibromo-ketone since the analytical value for bromine was low (Found: Br, 38·3. Calc. for $C_{15}H_{12}OBr_2$: Br, 43·8. Calc. for $C_{15}H_{13}OBr$: Br, 27·3%).

The residue was treated with collidine (20 ml.) and the mixture was heated on the steam-bath for 1 hr. The solvent was removed under reduced pressure, ether and water were added, and the ether solution was washed with dilute hydrochloric acid, dilute sodium hydrogen carbonate solution, and with water and dried (Na_2SO_4). Evaporation of the ether and evaporative distillation of the residue (bath, 190°/0·1 mm.) yielded the colourless *tropone* (II) (0·4 g.) as a slightly yellow oil (Found: C, 87·5; H, 4·75. $C_{15}H_{10}O$ requires C, 87·35; H, 4·9%). No ketonic derivatives could be prepared; a yellow-orange picrate, m. p. 116—121° (sealed tube), was obtained but could not be analysed.

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