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ALICYCLIC STUDIES—XII*

AN ALICYCLIC SYNTHESIS OF 2:3,6:7-DIBENZOTROPONE

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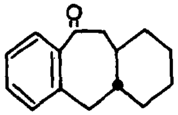
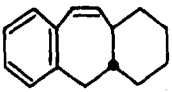
Abstract—*trans*-2-Benzylcyclohexylacetic acid was cyclised with polyphosphoric acid to give *trans*-2:3-benzo-5:6-cyclohexanocycloheptanone. Reduction to the corresponding alcohol followed by dehydration and dehydrogenation afforded 2:3,6:7-dibenzocyclohepta-3:4:6-triene, which was oxidized with selenium dioxide to 2:3,6:7-dibenzotropone.

THE reported preparation of *trans*-2-benzylcyclohexylacetic acid[1] has been improved experimentally, and cyclisation by means of polyphosphoric acid afforded a quantitative yield of *trans*-2:3-benzo-5:6-cyclohexanocycloheptanone (I). This ketone was reduced with sodium borohydride to the corresponding alcohol and the latter was dehydrated to the olefin (II) by naphthalene-β-sulphonic acid. Dehydrogenation by 30% palladised charcoal in the absence of solvent afforded 2:3,6:7-dibenzocyclohepta-2:4:6-triene (IIIa) identical with the Huang-Minlon reduction product of an authentic specimen of 2:3,6:7-dibenzotropone.[2] Attempts by various investigators to oxidise the triene (IIIa) to the ketone (IIIb) were unsuccessful.[3] Under various conditions (see experimental section), 9:10-anthraquinone is indeed obtained.[3] However, the oxidation to 2:3,6:7-dibenzotropone (IIIb) was effected in high yield through the use of freshly sublimed selenium dioxide in dry dioxane in a sealed tube at elevated temperature.


I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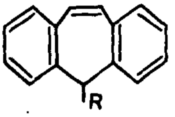
IIIa $R=H_2$
b $R=O$

EXPERIMENTAL†

1-*Benzoylcylclohexene* was prepared by the published procedure,[4] b.p. 147°/8 mm.

2-*Benzoylcyclohexylmalonic acid* was prepared by the published procedure, m.p. 190–191° (from carbon tetrachloride), as reported.[1] Decarboxylation yielded a mixture of 2-benzoylcyclohexylacetic acid and its benzyl ester, which could be saponified to the acid (total yield, 50%). The *acid* had m.p. 103–104°, as reported.[1] Infra-red absorption (chloroform): 1677 cm^{-1} (acetophenone C=O); 1711 cm^{-1} (C=O of saturated acid).

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* Part XI, Amiel and Ginsburg *Tetrahedron* **1** (1957).

† Melting-points are uncorrected.

[1] D. Ginsburg *J. Chem. Soc.* 2361 (1954).

[2] E. D. Bergmann and D. Ginsburg *Bull. Res. Council Israel* **1**, No. 3, 120 (1951).
E. D. Bergmann *et al. Bull. Soc. Chim. France* **18**, 684 (1951).

[3] W. Treibs and H. J. Klinkhammer *Chem. Ber.* **84**, 671 (1951); **83**, 367 (1950).

[4] R. E. Christ and R. C. Fuson *J. Amer. Chem. Soc.* **59**, 893 (1937).

2-*Benzylcyclohexylacetic acid* was prepared by Huang-Minlon reduction[5] of the keto-acid (16 g), using potassium hydroxide (12·4 g), hydrazine (100%; 7·6 ml) in diethylene glycol (90 ml). The acid (15·1 g) had b.p. 158–163°/0·5 mm, m.p. 74–75° (from light petroleum), as described previously.[1]

trans-2:3-*Benzo*-5:6-*cyclohexanocycloheptanone*

(a) *Intramolecular Friedel-Crafts cyclisation.* 2-Benzylcyclohexylacetic acid (17·8 g) was refluxed with thionyl chloride (45 ml) in dry benzene (100 ml) for 4 hr. After removal of benzene and excess thionyl chloride at the water-pump, dry carbon disulphide (100 ml), and anhydrous aluminium chloride (11·4 g) were added portionwise, and finally the mixture was boiled for 2 hr. After the usual workup, uncyclised acid (3·0 g) was recovered and the *ketone* was obtained by distillation (13·2 g; 83%), b.p. 142–146°/0·5 mm. Infra-red absorption (chloroform): 1671 cm^{-1} (C=O). Ultra-violet absorption: $\lambda\lambda_{\max}^{\mathrm{EtOH}}$ 2460–2470, 2870 Å; $\varepsilon\varepsilon_{\max}$ 7750, 1390.

The ketone was characterised as the yellow-orange 2:4-*dinitrophenylhydrazone* which formed prisms, m.p. 235·5–236·5° (from ethanol-ethyl acetate) (Found: C, 64·07; H, 5·61; N, 14·13. $C_{21}H_{22}O_4N_4$ requires C, 63·94; H, 5·62; N, 14·21%). Ultra-violet absorption: $\lambda_{\max}^{\mathrm{chf}}$ 3710 Å; $\varepsilon_{\max}$ 29,250.

The colourless *oxime* was formed in pyridine, m.p. 143·5–144·5° (from methanol) (Found: C, 78·42; H, 8·27; N, 6·12. C_{15}, $H_{19}ON$ requires C, 78·56; H, 8·35; N, 6·11%).

The colourless *semicarbazone* had m.p. 205° (from ethanol). Lit.[6] m.p. 205°. Ultra-violet absorption: $\lambda_{\max}^{\mathrm{chf}}$ 2580–2640 Å; $\varepsilon_{\max}$ 16,650.

(b) *Polyphosphoric acid cyclisation.* The acid (4 g) was stirred on the steam bath for 2 hr with polyphosphoric acid (80 g; Victor Chemical Co.). After the usual workup the same ketone as described in (a) was obtained in quantitative yield.

trans-2:3-*Benzo*-5:6-*cyclohexanocycloheptanol*

The ketone (10·7 g; 0·05 mole) was dissolved in methanol (125 g) and sodium borohydride (7·5 g; 0·2 mole) was added portionwise. After standing overnight, the mixture was worked up in the usual way and the *alcohol* was obtained in quantitative yield (10·7 g), m.p. 128–129° (from light petroleum) (Found: C, 83·20; H, 9·20. $C_{15}H_{20}O$ requires C, 83·24; H, 9·32%).

2:3:12:13:14:15-*Hexahydro*-2:3,6:7-*dibenzocyclohepta*-2:4-*diene*

The above alcohol (8·24 g) was dehydrated by boiling in toluene (125 ml) in the presence of naphthalene-β-sulphonic acid monohydrate (0·5 g). The theoretical quantity of water (0·7 ml) was obtained in the azeotropic collector during 1 hr. After the usual workup, the *olefin* was obtained as an oil, b.p. 106–108°/0·2 mm, which crystallised on cooling to form colourless needles, m.p. 37–38° (from methanol) (Found: C, 90·54; H, 9·00. $C_{15}H_{18}$ requires C, 90·91; H, 9·09%). Ultra-violet absorption: $\lambda_{\max}^{\mathrm{EtOH}}$ 2580 Å; $\varepsilon_{\max}$ 14,500.

2:3,6:7-*Dibenzocyclohepta*-2:4:6-*triene*

Refluxing the above olefin with an equal weight of 30% palladised charcoal in *p*-cymene for 6 hr under nitrogen afforded unreacted starting material.

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[5] Huang-Minlon *J. Amer. Chem. Soc.* **68**, 2487 (1946).

[6] J. Colonge and J. Sibeud *Compt. Rend.* **234**, 530 (1952).

A mixture of the olefin (1·5 g) and palladised charcoal (30%; 1·5 g) was heated under nitrogen for 5 hr at 300–320°. After cooling, benzene was added and the catalyst filtered. The catalyst was boiled several times with fresh portions of benzene, and filtered. The combined benzene extracts afforded after removal of the solvent, the *cycloheptatriene* (1·3 g), m.p. 130–131°; lit.[3] m.p. 130–131°. An authentic specimen of this compound was prepared by Huang-Minlon reduction[5] of 2:3,6:7-dibenzotropone, which was available from another synthetic route.[2] The m.p. of the triene thus obtained (130–131°) was undepressed upon admixture with the above triene. Ultra-violet absorption; $\lambda\lambda_{\max}^{\text{heptane}}$ 2530, 2860 Å; $\varepsilon\varepsilon_{\max}$ 5400, 13,650.

Attempted oxidations of triene to 2:3,6:7-*dibenzotropone*

(a) In analogy to fluorene oxidation,[7] to a boiling solution of the triene (0·5 g) in glacial acetic acid (1·2 ml) was added dropwise a solution of sodium dichromate (1·7 g) in glacial acetic acid (2·5 ml) and water (0·6 ml). Refluxing was continued for 2 hr; the orange solution turned green. After pouring into ice-water (20 ml) the mixture was allowed to stand for 2 hr and was then filtered. The solid had m.p. 262–270°, which was raised to 278° after recrystallisation from benzene. Sublimation afforded 9:10-*anthraquinone*, m.p. 283°, undepressed by an authentic specimen.

Heating the above mixture on the steam bath for only 1 hr afforded the quinone, while allowing it to stand at room temperature for 24 hr gave unreacted starting material even when a little benzene was added to produce a completely homogeneous solution.

(b) Attempted oxidation in a two-phase acetic acid-benzene system[8] afforded unreacted starting material.

(c) A mixture of the triene (0·42 g), dry dioxane (7·5 ml), and selenous acid (0·33 g; 1·1 mole) was refluxed for 36 hr. After removal of selenium by filtration (*c.* 20% of the theoretical amount), sulphur dioxide was bubbled through the filtrate; red colloidal selenium was obtained and was coagulated by boiling. After filtration and evaporation of the dioxane, the residue was chromatographed on alumina (light petroleum). The starting material was largely recovered and *anthraquinone* (12 mg) was again isolated. The use of freshly sublimed selenium dioxide or higher-boiling solvents such as xylene or acetic anhydride did not lead to the desired product.

2:3,6:7-*Dibenzotropone* was finally obtained by heating, in a sealed tube, a mixture of the triene (0·5 g), dry dioxane (10 ml), and freshly sublimed selenium dioxide at 160° for 6 hr. After cooling, the black selenium was filtered (0·17 g; theory 0·21 g) and the dioxane was evaporated. The residue (0·55 g) had m.p. 88° after trituration with ether. It had m.p. 89° (from methanol), undepressed upon admixture with an authentic specimen, m.p. 89°. It gave an orange-red 2:4-*dinitrophenylhydrazone*, m.p. 258°. Lit.[9] m.p. 258°.

The same reaction mixture even after 48 hr boiling in an open vessel afforded mainly recovered starting material.

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[7] E. H. Huntress, E. B. Hershberg and I. S. Cliff *J. Amer. Chem. Soc.* **53**, 2720 (1931).
[8] Y. Mazur, E. Koller, O. Jeger and L. Ruzicka *Helv. Chim. Acta* **35**, 181 (1952).
[9] E. D. Bergmann and D. Ginsburg *Chem. and Ind.* 45 (1954).