Tetrahedron, 1957, Vol. 1, pp. 9–18. Pergamon Press Ltd., London

ALICYCLIC STUDIES—XI*

ATTEMPTED SYNTHESES OF 5:6-BENZAZULENE AND BENZHEPTALENES

YAACOV AMIEL and DAVID GINSBURG
Daniel Sieff Research Institute, Rehovot; Israel Institute of Technology, Haifa

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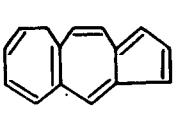
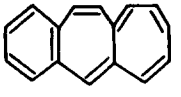
Abstract—1-Benzoylcyclopentene was used as starting material in an alicyclic approach towards the synthesis of 5:6-benzazulene. Bromination-dehydrobromination of the intermediate *trans*-1:2:3:4:9:10 hexahydrobenzazulene afforded a dibromo- and tetrabromo-derivative of 5:6-benzazulene. The bromination-dehydrobromination method is not feasible for the dehydrogenation of hydrobenzheptalenes to the as yet unknown benzheptalene system.

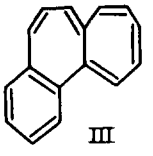
SUCCESSFUL alicyclic approaches to 4:5-benzazulene have been reported.[1, 2] 1-Benzoylcyclopentene appeared to be a useful starting material for the synthesis of the known 5:6-benzazulene[3] (I), while its seven-membered homologue might conceivably lead to the as yet unknown 2:3-benzheptalene (II). Another alicyclic intermediate, 2-phenylcyclohept-2-enone[4] might afford a route to 1:2-benzheptalene (III).



I

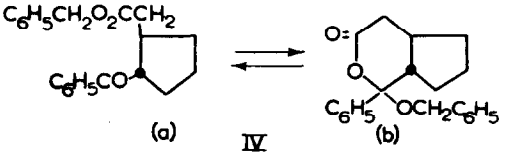


II

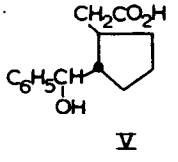


III

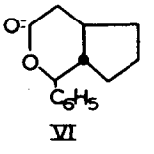
Michael condensation of 1-benzoylcyclopentene with dibenzyl malonate[5] afforded an adduct which upon debenzylation with hydrogen bromide in glacial acetic acid[6] at room temperature yielded the half ester. It is interesting that the monobenzyl ester (IVa) obtained upon decarboxylation exists in part in the form of the pseudo-ester (IVb) as evidenced by its infra-red spectrum. (See experimental section.) The same situation



(a) IV (b)



V

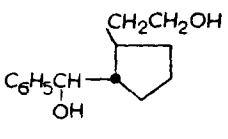


VI

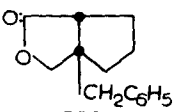
* Part X. *Tetrahedron* **1**, (1957).
[1] J. R. Nunn and W. S. Rapson *J. Chem. Soc.* 1051 (1949).
[2] Y. Amiel, A. Löffler, and D. Ginsburg *J. Amer. Chem. Soc.* **76**, 3625 (1954).
[3] A. Plattner, A. Fürst and W. Keller *Helv. Chim. Acta* **32**, 2464 (1949).
[4] D. Ginsburg and R. Pappo *J. Amer. Chem. Soc.* **75**, 1094 (1953).
[5] D. Ginsburg *J. Chem. Soc.* 2361 (1954).
[6] D. Ben-Ishai and A. Berger *J. Org. Chem.* **17**, 1564 (1952).

obtains in the seven-membered ring homologue (see below). Complete debenzylation can be effected by employing the acidic reagent at elevated temperature. Decarboxylation of the malonic acid thus obtained followed by Huang-Minlon reduction afforded *trans*-2-benzylcyclopentylacetic acid.[5]

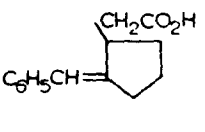
On one occasion, when catalytic hydrogenolysis of the dibenzyl ester was attempted,[4] decarboxylation of the acidic reaction products led to a mixture of acidic material (*trans*-2-benzoylcyclopentylacetic acid) and neutral material. It was clear from the behaviour of the latter on alkaline treatment and from its infra-red spectrum that this was a δ-lactone (absorption at 1746 cm^{-1}). Presumably the ketonic function was reduced in part of the material undergoing hydrogenolysis and the unisolated *trans*-acid (V) afforded the crystalline δ-lactone (VI). That this was indeed the case was shown by lithium aluminium hydride reduction to the crystalline *trans*-diol (VII).



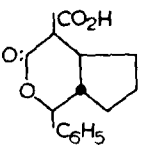
VII



VIII



IX



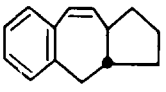
X

Further evidence on this point was sought by sodium borohydride reduction of IVa or of the corresponding free acid, *trans*-2-benzoylcyclopentylacetic acid. Thus, it was hoped that the hydroxy-ester or hydroxy-acid (V) would lead to the same lactone (VI). However, the hydroxy-ester upon alkaline saponification was converted into the same *stable* hydroxy-acid which was formed directly by sodium borohydride reduction of *trans*-2-benzoylcyclopentylacetic acid. Whilst a δ-lactone was formed during decarboxylation of the hydrogenolysis reaction mixture, the pure hydroxy-acid (V) upon treatment with naphthalene-β-sulphonic acid gave a γ-lactone (VIII) (infra-red absorption at 1765 cm^{-1}). The two five-membered rings in the γ-lactone must be *cis*-fused for steric reasons so that the *trans*-product formed after Michael condensation must eventually pass through the intermediate (IX) in which the *trans*-stereochemistry is destroyed. That the driving force in this reaction is the formation of the more stable γ-lactone was shown by refluxing the δ-lactone with sulphuric acid in acetic acid. The latter was quantitatively converted to a product whose infra-red spectrum was identical with that of the γ-lactone. The formation of the δ-lactone may be finally rationalised by the suggestion that it is not formed by lactonization of (V) after decarboxylation of the hydrogenolysis reaction mixture, but rather that X is formed in the hydrogenolysis mixture from the hydroxy-malonic acid and this upon decarboxylation affords the δ-lactone (VI). Since the employment of hydrogen bromide in glacial acetic acid became the method of choice for debenzylation, the structures of the lactones were not further investigated.

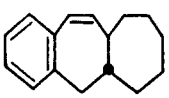
Polyphosphoric acid converted *trans*-2-benzylcyclopentylacetic acid into *trans*-7 oxo-1:2:3:4:7:8:9:10-octahydro-5:6-benzazulene in quantitative yield.[7] Sodium borohydride reduction afforded the corresponding alcohol,[7] and dehydration of the latter gave *trans*-1:2:3:4:9:10-hexahydrobenzazulene (XI).

[7] J. W. Cook, N. A. McGinnis, and S. Mitchell *J. Chem. Soc.* 286 (1944). See also ref. 5.

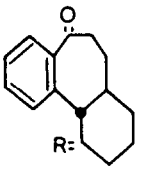
Rather than employing a high-temperature dehydrogenation method, stepwise bromination-dehydrobromination of this olefin was attempted. It soon became clear, however, that even when only one mole of *N*-bromosuccinimide is used, completely dehydrogenated products are obtained. After this bromination, chromatography on



XI



XII



XIII (a) R=H_2
(b) R=O

alumina permitted recovery of the major portion of the starting material (XI) and isolation of an alicyclic bromo-derivative and two bromo-derivatives of 5:6-benzazulene, a deep-purple dibromo-compound and a green-violet tetrabromo-derivative. On the basis of Anderson's work on bromination of azulene,[8] the dibromo-derivative is tentatively formulated as 1:3-dibromo-5:6-benzazulene.

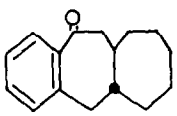
Concurrently with the work described above, 1-benzoylcycloheptene was analogously converted to the corresponding olefin, *trans*-1:6:7:8:9:10:11:12-octahydro-2:3-benzheptalene (XII). Furthermore, *trans*-3-oxo-2-phenylcycloheptylacetic acid[4] was converted by the Arndt-Eistert procedure to the corresponding keto-propionic acid and a small quantity of unreacted starting material was removed by treatment with anhydrous hydrogen fluoride. The substituted acetic acid is quantitatively cyclised to yield a neutral diketone,[4] whereas the keto-propionic acid is unaffected by this reagent. The keto-propionic acid was then cyclised by means of polyphosphoric acid to give *trans*-3:10-dioxo-3:4:5:6:7:8:9:10:11:12-decahydro-1:2-benzheptalene (XIIIb). *trans*-2-Phenylcycloheptylpropionic acid was similarly cyclised to the monoketone, XIIIa. Since *trans*-adducts are obtained in the Michael condensation of 2-aryl-cycloalk-2-enones[2, 4, 9] and since the stereochemistry would remain unchanged during the Arndt-Eistert reaction,[10] the propionic acids and XIIIa and XIIIb described above still maintain *trans*-stereochemistry. Ketone XIIIa and the isomeric product prepared by Gutsche[11] are both oils, but they give different semicarbazones (see experimental section). Gustsche's isomer must therefore be the *cis*-compound.

Bromination of XII under various reaction conditions, followed by dehydrobromination, led to an intractable mixture of bromo-derivatives. This method was therefore abandoned in the attempt to obtain 1:2- and 2:3-benzheptalene. Other methods to effect the synthesis of these as yet unknown compounds, are under investigation.

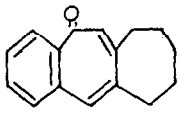
Bromination of *trans*-4-oxo-1:4:5:6:7:8:9:10:11:12-decahydro-2:3-benzheptalene (XIV) with one mole of *N*-bromosuccinimide followed by dehydrobromination, afforded a ketone (XV) in addition to recovered starting material, which is formulated as a tropone even though it forms a 2:4-dinitrophenylhydrazone. A study of models

[8] A. G. Anderson Jr., J. A. Nelson, and J. J. Tazuma *J. Amer. Chem. Soc.* **75**, 4980 (1953).
[9] D. Ginsburg and R. Pappo *J. Chem. Soc.* 938 (1951).
[10] C. D. Gutsche *J. Amer. Chem. Soc.* **70**, 4150 (1948).
[11] C. D. Gutsche *J. Amer. Chem. Soc.* **73**, 786 (1951).

shows that XV cannot be coplanar, so that the formation of this derivative is another case in which a tropone gives a ketonic derivative. The ultra-violet absorption supports this formulation and is analogous to spectral data obtained in related systems.[12]



XIV



XV

EXPERIMENTAL*

1-Benzoylcyclopentene was prepared by the published procedure,[13] b.p 117–125°/1 mm.

Michael condensation with dibenzyl malonate was carried out as reported,[5] using 1-benzoylcyclopentene (58 g), dibenzyl malonate (116 g), and potassium *tert.*-butoxide [from potassium (1·35 g) and *tert.*-butanol (21·5 ml)]. After 3 hr at 60° with occasional shaking and standing overnight at room temperature, acetic acid (3 ml) and ethyl acetate (480 ml) were added. Apparently because of traces of sulphur compounds from the preparation of the acceptor, the mixture must be refluxed for 4 hr over Raney nickel (20–30 g). After filtration, hydrogenolysis is effected, using palladised charcoal (10%; 10·6 g) at an initial pressure of 60 lb/sq. in. and 55°. When 2 moles of hydrogen had been absorbed, the catalyst was removed by filtration and the solution extracted with 10% aqueous sodium carbonate. After the usual workup,[4] *benzoylcyclopentane* (35 g) formed by reduction of unreacted starting material, b.p. 92–97°/1·5 mm;[14] n_D^{20} 1·5426[15] and trans-2-*benzoylcyclopentylmalonic acid* (*c.* 40 g), m.p. 144–145° (from carbon tetrachloride), were obtained, Lit. m.p. 144–145°.[5] The acidic fraction also contains the half benzyl ester of the malonic acid (*c.* 17 g).

Since reduction of 1-benzoylcyclopentene, at the expense of hydrogenolysis of the benzyloxy groups, could not be avoided, this method of debenzylation was abandoned in favour of hydrogen bromide in glacial acetic acid.[6, 16]

For the scale described above, a solution of hydrogen bromide in acetic acid (33%; 300 ml) is added to the reaction mixture. After standing overnight at room temperature, only one benzyl group is removed, since decarboxylation of the acidic material thus obtained affords trans-*benzyl* 2-*benzoylcyclopentyl acetate* identical with material described below. However, refluxing the mixture for 4 hr affords the free *malonic acid*. By this method, of course, unreacted 1-benzoylcyclopentene can be recovered.

Decarboxylation of hydrogenolysis product was effected by heating at 180–190° for 20 min. The trans-2-*benzoylcyclopentylacetic acid* had b.p. 133–138°/0·5 mm and formed colourless plates, m.p. 66–67° (from carbon tetrachloride) (Found: C, 72·09; H, 7·17. $C_{14}H_{16}O_3$ requires C, 72·39; H, 6·94%). Infra-red absorption (chloroform): 1677 cm^{-1} (acetophenone type C=O); 1711 cm^{-1} (C=O of saturated acid).

* M.p.'s. and b.p.'s are uncorrected.

[12] D. Ginsburg and W. J. Rosenfelder *Tetrahedron* **1**, (1957).

[13] R. C. Fuson, R. Johnson, and W. Cole *J. Amer. Chem. Soc.* **60**, 1594 (1938).

[14] D. Y. Curtin and S. Schmukler *J. Amer. Chem. Soc.* **77**, 1105 (1955).

[15] F. S. Bridson-Jones and G. D. Buckley *J. Chem. Soc.* 3015 (1951).

[16] Y. Klibansky and D. Ginsburg *J. Chem. Soc.* 1293 (1957).

In addition a neutral product was obtained by decarboxylation of the half ester trans-*benzyl 2-benzoylcyclopentyl acetate*, b.p. 190–200°/1·4 mm (Found: C, 73·50; H, 7·90. $C_{21}H_{22}O_3$ requires C, 73·82; H, 7·74%). Infra-red absorption (chloroform): 1677 cm^{-1} (weak band, acetophenone C=O); 1731 cm^{-1} (C=O of saturated ester); 1170, 1160 cm^{-1} (pseudo-ester in ether region).

The ester gave a yellow-orange 2:4-*dinitrophenylhydrazone*, m.p. 124–125° (from ethanol) (Found: C, 64·70; H, 4·96; N, 11·09. $C_{27}H_{26}O_6N_4$ requires C, 64·53; H, 5·22; N, 11·15%).

Refluxing the ester (3 g) with ethanolic (30 ml) potassium hydroxide (10 g) for 2 hr affords the acetic acid (2·1 g), m.p. 66–67°. The overall yield of the acetic acid from the Michael condensation is therefore 52%.

δ-Lactone (VI)

On occasion, decarboxylation of the acidic product of hydrogenolysis afforded a *neutral compound* which formed colourless leaves, m.p. 109° (from ether). It gave no ketonic derivatives. Infra-red absorption (chloroform): 1746 cm^{-1} (δ-lactone) (Found: C, 77·58; H, 7·46. $C_{14}H_{16}O_2$ requires C, 77·75; H, 7·42%). The compound was soluble in 10% sodium hydroxide solution after 30 min boiling, but was recovered unchanged upon acidification of the alkaline solution.

Diol (VII)

A mixture of the δ-lactone (1 g), lithium aluminium hydride (200 mg), and dry ether (200 ml) was heated on the steam bath for 2 hr. After the usual workup, using alkali to decompose the reaction mixture, evaporation of the ether afforded glistening colourless leaves of the *diol*, m.p. 120° (from ether) (Found: C, 76·12; H, 9·20; Zerewitinoff, 1·97. $C_{14}H_{20}O_2$ requires C, 76·32; H, 9·15%; Zerewitinoff, 2·0).

Sodium borohydride reduction of trans-*2-benzoylcyclopentylacetic acid*

Sodium borohydride (0·5 g) was added portionwise to a solution of the keto-acid (0·5 g) in methanol (10 ml) and the mixture was permitted to stand overnight. After the usual workup, the *hydroxy-acid* (*V*) was obtained, m.p. 108·5° (from carbon tetrachloride) (Found: C, 71·78; H, 7·80; Zerewitinoff, 2·01. $C_{14}H_{18}O_3$ requires C, 71·77; H, 7·74%; Zerewitinoff, 2·0). The same hydroxy-acid was obtained by reduction of the keto-benzyl ester with sodium borohydride. The hydroxy-ester thus obtained exhibited bands at 1731 cm^{-1} (C=O of saturated ester) and 3460 cm^{-1} (secondary OH) in its infra-red spectrum. Alkaline hydrolysis afforded the hydroxy-acid described above.

γ-Lactone (VIII)

(a) The above hydroxy-acid was refluxed in toluene in the presence of naphthalene-β-sulphonic acid; the theoretical quantity of water expected was collected in an azeotropic collector. After removal of the catalyst and solvent, the *γ-lactone* was obtained as a colourless oil which showed a band at 1765 cm^{-1} (*γ-lactone*) in its infra-red spectrum. (b) A product completely identical in infra-red spectrum with that obtained above was formed by heating the hydroxy-acid on the steam bath with 50%

sulphuric acid for 1 hr. (c) The δ-lactone (50 mg) was refluxed with sulphuric acid (50%; 1 ml) in acetic acid (3 ml) for 48 hr. After dilution with water and ether extraction, drying (sodium sulphate), and removal of the ether, the colourless *γ-lactone* was obtained, again identical in infra-red spectrum with the products described in (a) or (b) above.

trans-2-*Benzylcyclopentylacetic acid*

2-Benzoylcyclopentylacetic acid (25 g) was reduced by the Huang-Minlon procedure,[17] using potassium hydroxide (20·4 g), hydrazine hydrate (85%; 12·4 ml) in diethylene glycol. The *acid* product (22·3 g; 95%) had b.p. 160–166°/0·5 mm, m.p. 53–54° (from light petroleum) (Found: C, 77·33; H, 8·53. $C_{14}H_{18}O_2$ requires C, 77·03; H, 8·31%).

trans-7-*Oxo*-1:2:3:4:7:8:9:10-*octahydro*-5:6-*benzazulene*

(a) *Intramolecular Friedel-Crafts cyclisation.* 2-Benzylcyclopentylacetic acid (7·6 g) was converted into its acid chloride in the usual way by using thionyl chloride (15 ml) in dry benzene (40 ml). After refluxing for 4 hr the excess thionyl chloride and the benzene were removed at the water-pump. The acid chloride was dissolved in dry carbon disulphide (40 ml) and aluminium chloride (4·75 g; 1·1 mole) was added portionwise with cooling. The mixture was then refluxed for 2 hr and allowed to stand overnight. After the usual workup, uncyclised acid (2·9 g) was recovered and the neutral fraction was distilled. The desired *ketone* had b.p. 120–123°/0·3 mm (4·5 g; 65%) and crystallised spontaneously after distillation, m.p. 56° (from methanol); Lit.[7] m.p. 56°. Infra-red absorption (chloroform): 1675 cm^{-1} (C=O). Ultra-violet absorption: $\lambda\lambda_{max}^{EtOH}$ 2450, 2810 Å. $\varepsilon\varepsilon_{max}$ 6300, 1160.

The 2:4-*dinitrophenylhydrazone* formed orange rhombic plates, m.p. 194–196° (from ethanol-ethyl acetate); Lit. m.p. 184–185°, 169–170°, respectively[5, 7] (Found: C, 63·50; H, 5·32. Calc. for $C_{20}H_{20}O_4N_4$: C, 63·15; H, 5·30%). Ultra-violet absorption: λ_{max}^{chf} 3690 Å; ε_{max} 25,200.

The *oxime* was prepared by the pyridine method, m.p. 153·5–154·5° (from methanol) (Found: C, 78·38; H, 8·34; N, 6·37. $C_{14}H_{17}ON$ requires C, 78·10; H, 7·96; N, 6·51%).

The semicarbazone had m.p. 210–211° (from ethanol) (Found: N, 16·30. $C_{15}H_{19}ON_3$ requires N, 16·33%). Ultra-violet absorption: λ_{max}^{chf} 2550 Å; ε_{max} 9250.

(b) *Polyphosphoric acid cyclisation.* A mixture of the acid (4 g) and polyphosphoric acid (80 g; Victor Chemical Co.) was heated on the steam bath with vigorous mechanical stirring for 2 hr. After cooling and pouring on ice, the organic material was extracted with ether. The ether solution was washed with 5% sodium hydroxide to remove uncyclised acid (0·1 g). Removal of the ether afforded the ketone, identical with that described in (a) (3·85 g; 96%).

trans-7-*Hydroxy*-1:2:3:4:7:8:9:10-*octahydro*-5:6-*benzazulene*

The above ketone (10 g) was reduced in the usual way with sodium borohydride (7·5 g) in methanol (125 ml). The *alcohol*, m.p. 128° (from light petroleum) was obtained in quantitative yield; Lit. m.p. 128°.[7] Infra-red absorption (chloroform): 3460 cm^{-1} (secondary OH).

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

trans-1:2:3:4:9:10-*Hexahydro-5:6-benzazulene*

A mixture of the above alcohol (5 g), dry toluene (100 ml), and naphthalene-β-sulphonic acid monohydrate (0·5 g) was refluxed. The theoretical amount of water expected (0·45 ml) was obtained in the azeotropic collector during 1 hr. After the usual workup, the *olefin* is obtained, m.p. 33–35° (without recrystallisation). Lit.[7] m.p. 29–35°. Ultra-violet absorption: $\lambda\lambda_{max}^{EtOH}$ 2600 Å; ε_{max} 10,500.

Aromatization with N-*bromosuccinimide*

A mixture of 1:2:3:4:9:10-hexahydro-5:6-benzazulene (4 g), dry carbon tetrachloride (70 ml) and powdered *N*-bromosuccinimide (4·25 g; 1·1 mole) was refluxed for 2 hr. After cooling, the succinimide floating on top of the solvent was filtered and the solvent was removed from the filtrate at the water pump. Some hydrogen bromide evolution was observed, 2:6-lutidine (70 ml) was added to the residue, and the mixture was refluxed for 4 hr. Most of the solvent was removed at the water pump. Water was added to the residue and the mixture was extracted with ether. The ether extract was washed with dilute hydrochloric acid and the ether solution was dried (sodium sulphate) and the solvent was removed. The residue was practically all recovered starting material together with a small amount of highly-coloured material which could not be isolated.

The bromination was therefore repeated, but without the lutidine treatment. The bromination residue was taken up in light petroleum and chromatographed on alumina (Merck, acid-washed). The first and major fraction obtained (3·8 g) was starting material. The second fraction was a hydro-5:6-benzazulene, m.p. 188–189° (from light petroleum), whose exact structure could not be determined because it was formed in very small quantity. Its ultra-violet absorption did not show more extended conjugation than was present in the starting material. The third fraction was a colourless dibromohydro-5:6-benzazulene, m.p. 72° (from pentane) (Found: C, 48·89; H, 4·58; Br, 46·65. $C_{14}H_{14}Br_2$ requires C, 49·15; H, 4·12; Br, 46·73%).

A deep-purple product (0·2 g) was then obtained in needles, m.p.>360°; the compound decomposes during heating. This product was purified by formation of its complex with trinitrobenzene, m.p. 118–121°. The complex decomposed on alumina and afforded long deep-purple needles (Found: C, 50·8; H, 2·3; Br, 48·7. $C_{14}H_8Br_2$ requires C, 50·0; H, 2·4; Br, 47·6%). This product is formulated as 1(?):3(?)-*dibromo-5:6-benzazulene*. Ultra-violet absorption: $\lambda\lambda_{max}^{iso\text{-}octane}$ 2580, 3080, 3620, 3800, 4000, 5850 Å; $\varepsilon\varepsilon_{max}$ 25,850, 64,850, 6850, 7450, 7350, 1000.

The final product isolated (0·3 g) formed short green-violet needles, m.p. 224–226° (from dioxane) is a *tetrabromo-5:6-benzazulene* (Found: C, 35·0; H, 1·4; Br, 63·5. $C_{14}H_6Br_4$ requires C, 34·0; H, 1·2; Br, 64·8%). Ultra-violet absorption: $\lambda\lambda_{max}^{iso\text{-}octane}$ 2540, 3175–3240, 3570, 3750–3770, 3940, 4140–4150, 5050–5100, 5500, 5600, 5750, 5850 Å; $\varepsilon\varepsilon_{max}$ 22,000, 70,700, 5150, 6200, 5750, 4100, 575, 850, 825, 900, 875. These values for the two bromo-compounds may be compared with those obtained for 5:6-benzazulene, the parent hydrocarbon whose ultra-violet absorption[3] follows: $\lambda\lambda_{max}^{iso\text{-}octane}$ 2500, 2800, 3530, 3700, 5500–5700, 5820 Å; $\varepsilon\varepsilon_{max}$ 18,000, 56,000, 4000, 2950, strong, strong. As expected, the bromo-derivatives exhibit a bathochromic shift in their spectra.

1-*Benzoylcycloheptane* was prepared by the published procedure,[5] b.p. 155°/8 mm.

trans-2-*Benzoylcycloheptylmalonic acid* was prepared in exact analogy to the

cyclopentyl analogue described above, m.p. 169–170° (from carbon tetrachloride). Decarboxylation of the hydrogenolysis reaction mixture, as above, gave *2-benzoylcycloheptylacetic acid*, b.p. 190–194°/0·2 mm, m.p. 95–96° (from heptane) (Found: C, 73·90; H, 7·75. $C_{16}H_{20}O_3$ requires C, 73·82; H, 7·74%). It was accompanied by its *benzyl ester*, b.p. 145–155°/0·2 mm, which exhibited in its infra-red spectrum weak bands at 1677 cm^{-1} and 1731 cm^{-1} and strong bands at 1170 and 1160 cm^{-1}, indicating the presence of a large proportion of pseudo-ester. The ester was saponified to the free acid by boiling with hydrogen bromide in acetic acid for 2 hr. The overall yield of the acetic acid from the Michael condensation was thus 53%.

trans-2-*Benzylcycloheptylacetic acid* was prepared in nearly quantitative yield in analogy to the cyclopentyl analogue from the keto-acid (25 g), potassium hydroxide (18·6 g), hydrazine (100%; 11·5 ml), and diethylene glycol (133 ml). The *acid* had b.p. 166–169°/0·5 mm and m.p. 63·5–64·5° (from pentane) (Found: C, 78·10; H, 9·00. $C_{16}H_{22}O_2$ requires C, 78·01; H, 9·00%).

trans-4-*Oxo*-1:4:5:6:7:8:9:10:11:12-*decahydro*-2:3-*benzheptalene*

The ketone was prepared by intramolecular cyclisation of the acid chloride with aluminium chloride in carbon disulphide (see above). The acid (17·8 g) gave a small amount of recovered uncyclised acid (3·7 g) and the oily *ketone* (13·3 g, 81%), b.p. 152–160°/0·6 mm. Infra-red absorption (chloroform): 1668 cm^{-1} (C=O). Ultra-violet absorption: $\lambda\lambda_{max}^{EtOH}$ 2470–2490, 2870–2910 Å; $\varepsilon\varepsilon_{max}$ 9280, 1750.

The ketone was also prepared quantitatively in analogy to its five-membered homologue by cyclization with polyphosphoric acid. It was characterised as the orange 2:4-*dinitrophenylhydrazone*, m.p. 247–248° (from ethanol-ethyl acetate) (Found: C, 64·90; H, 6·07; N, 13·57. $C_{22}H_{24}O_4N_4$ requires C, 64·69; H, 5·92; N, 13·72%). Ultra-violet absorption: λ_{max}^{chf} 3770 Å; ε_{max} 25,500.

The *oxime* was prepared in pyridine and formed colourless crystals, m.p. 155–156° (from methanol) (Found: C, 78·85; H, 8·38; N, 5·67. $C_{16}H_{21}ON$ requires C, 78·97; H, 8·70; N, 5·76%).

The colourless *semicarbazone* had m.p. 202–203° (from ethanol) (Found: C, 71·07; H, 7·88; N, 14·83. $C_{17}H_{23}ON_3$ requires C, 71·54; H, 8·12; N, 14·73%). Ultra-violet absorption: λ_{max}^{chf} 2580–2680 Å; ε_{max} 19,400.

trans-4-*Hydroxy*-1:4:5:6:7:8:9:10:11:12-*decahydro*-2:3-*benzheptalene*.

The ketone (10 g) was reduced in methanol (100 ml) with sodium borohydride (6·5 g) in the usual way. The *alcohol* was obtained in quantitative yield, m.p. 108–109° (from light petroleum) (Found: C, 83·20; H, 9·70. $C_{16}H_{22}O$ requires C, 83·42; H, 9·63%).

trans-1:6:7:8:9:10:11:12-*Octahydro*-2:3-*benzheptalene*.

The alcohol (6·6 g) in toluene (120 ml) containing naphthalene-β-sulphonic acid monohydrate (0·6 g) afforded after 1 hr of reflux the expected amount of water (0·5 ml). After the usual workup the *olefin* was obtained as an oil, b.p. 122–126°/0·2 mm; $n_D^{21.5}$ 1·5794. Ultra-violet absorption: λ_{max}^{EtOH} 2540 Å; ε_{max} 14,860.

Bromination experiments

(a) The olefin (2·9 g) was refluxed in dry carbon tetrachloride (60 ml) with powdered *N*-bromosuccinimide (2·47 g; 1·1 mole) for 45 min. At this time the reaction

was over and hydrogen bromide could be observed. After the usual workup, the reaction mixture was distilled, b.p. 130°/0·3 mm. The ultra-violet spectrum showed this was mainly starting material, but the analysis showed the material contained *c.* 20% bromine. Chromatography of the product before or after dehydrobromination did not permit isolation of pure material. Use of excess NBS in brominations with the hope that completely aromatised material could be isolated, failed.

(b) Bromination of 4-*oxo*-1:4:5:6:7:8:9:10:11:12-*decahydro*-2:3-*benzheptalene*—A mixture of the ketone (4·1 g), dry carbon tetrachloride (50 ml) and NBS (3·56 g; 1 mole) was refluxed. Reaction was complete after 1 hr. Dehydrobromination was effected with 2:6-lutidine. After the usual workup, distillation afforded the starting material (3·3 g) and a fraction of a *ketone* b.p. 193°/0·3 mm (0·5 g). This crystallised after standing, m.p. 86–88° (from light petroleum). Infra-red absorption (chloroform): 1626, 1578 cm^{-1} (tropone C=O). Ultra-violet absorption: $\lambda\lambda_{max}^{EtOH}$ 2300, 3200, 3500 Å; $\varepsilon\varepsilon_{max}$ 31,000, 6400, 5800. The ketone gave a 2:4-*dinitrophenylhydrazone* which formed short brownish-crimson needles, m.p. 242·5–243° (from ethanol-ethyl acetate) (Found: C, 65·43; H, 4·74; N, 13·72. $C_{22}H_{20}O_4N_4$ requires C, 65·40; H, 4·95; N, 13·86%). Ultra-violet absorption: λ_{max}^{chf} 4000 Å; ε_{max} 26,700.

trans-3-*Oxo*-2-*phenylcycloheptylacetic acid* was prepared by the published procedure,[4] m.p. 115° (from benzene). Lit.[4] m.p. 115°. trans-2-*Phenylcycloheptylacetic acid* was prepared from the keto-acid (8 g) by the Huang-Minlon method,[17] using potassium hydroxide (6·2 g), hydrazine (3·8 ml; 100%) in diethylene glycol (45 ml), in almost quantitative yield, as an oil which solidified upon trituration with light petroleum, m.p. 68° (from hexane). Lit.[4] m.p. 68–69°. This procedure is better than the published preparation by Clemmensen reduction.[4]

trans-3-*Oxo*-2-*phenylcycloheptylpropionic acid*

A mixture of the acetic acid (13 g), dry benzene (50 ml), and thionyl chloride (80 ml) was refrigerated for 48 hr.[18] The excess solvents were removed in a high vacuum. Dry benzene was again added and removed in a high vacuum to help remove traces of thionyl chloride. The acid chloride was then dissolved in dry benzene (10 ml) and dry ether (10 ml) and the solution was added to an ether solution containing diazomethane (14·5 g) at 0°. After 2 hr the solvents and excess of diazomethane were removed by distillation and the residue was dissolved in hot absolute ethanol (100 ml) and treated portionwise with dry freshly precipitated silver oxide (10 g). The mixture was refluxed for 3 hr while nitrogen was evolved. Charcoal (3 g) was added and boiling was continued for 15 min. The mixture was then cooled and filtered. Saponification of the ester thus obtained was effected by adding potassium hydroxide (*c.* 10 g) to the solution and refluxing for 4 hr. After the usual workup, acidic material was isolated (9·9 g). Separation between the propionic acid and unreacted acetic acid was accomplished by treating the mixture of acids with anhydrous hydrogen fluoride (*c.* 200 ml). The acetic acid was quantitatively cyclised and gave *trans*-5:11-dioxo-6:6a:7:8:9:10:11:11a-octahydro-5H-cyclohepta[a]naphthalene, m.p. 106° (from light petroleum).[4] The *propionic acid* remained unchanged and was obtained as a viscous oil (6·7 g; 50%) which crystallised on standing, m.p. 116–118° (from light petroleum) (Found: C, 73·40; H, 7·50. $C_{16}H_{20}O_3$ requires C, 73·82; H, 7·74%).

[18] D. Ginsburg and R. Pappo *J. Chem. Soc.* 1524 (1953).

trans-2-*Phenylcycloheptylpropionic acid*

As there was no possibility, in this case, of obtaining an enol lactone during the treatment with thionyl chloride, the corresponding acetic acid was converted to the acid chloride by refluxing with thionyl chloride in dry benzene. The Arndt-Eistert reaction and workup were carried out exactly as just described for the keto-acid. In this case, hydrogen fluoride treatment caused conversion of unreacted acetic acid to *trans*-5-oxo-6:6a:7:8:9:10:11:11a-octahydro-5H-cyclohepta[a]naphthalene, m.p. 60–61°, whilst the *propionic acid* was unchanged in this treatment and was obtained as a yellow oil, b.p. 152–158°/0·5 mm (55% yield) (Found: neut. equiv., 250. $C_{16}H_{22}O_2$ requires 246). The *methyl ester* prepared by diazomethane esterification of the acid was an oil, b.p. 167°/2 mm.

trans-3-*Oxo*-3:4:5:6:7:8:9:10:11:12-*decahydro*-1:2-*benzheptalene*

The propionic acid just described (2·5 g) was converted through the acid chloride exactly as described for the five-membered homologue (see above) to the ketone (1·05 g). A part of the propionic acid was recovered (0·7 g). The same *ketone* was obtained in nearly quantitative yield by cyclisation with polyphosphoric acid in the usual way. It was an oil, b.p. 190°/0·4 mm. Infra-red absorption (chloroform): 1669 cm^{-1} (C=O). Ultra-violet absorption: $\lambda\lambda_{max}^{EtOH}$ 2500, 2770–2860 Å; $\varepsilon\varepsilon_{max}$ 9500, 1700.

It was characterised as the colourless *semicarbazone*, m.p. 204° (from ethanol) (Found: N, 14·60. $C_{17}H_{23}ON_3$ requires N, 14·73%). Ultra-violet absorption: λ_{max}^{chf} 2580–2600 Å; ε_{max} 19,400. Gutsche[11] reports m.p. 239–240° for the isomeric semicarbazone, which must therefore be the derivative of the *cis*-isomer.

The yellow-orange 2:4-*dinitrophenylhydrazone* had m.p. 209–211° (from ethanol) (Found: N, 13·40. $C_{22}H_{24}O_4N_4$ requires N, 13·72%). Ultra-violet absorption: λ_{max}^{chf} 3650 Å; ε_{max} 24,000.

trans-3:10-*Dioxo*-3:4:5:6:7:8:9:10:11:12-*decahydro*-1:2-*benzheptalene*

The keto-propionic acid was converted into the diketone by intramolecular cyclisation of its acid chloride in the usual way. The *diketone* was obtained as an oil which after purification by chromatography on alumina solidified upon refrigeration, but was liquid at room temperature (Found: C, 79·10; H, 7·70. $C_{16}H_{18}O_2$ requires C, 79·31; H, 7·49%). Infra-red absorption (chloroform): 1705 cm^{-1} (alicyclic C=O); 1669 cm^{-1} (C=O adjacent to aromatic nucleus). Ultra-violet absorption: $\lambda\lambda_{max}^{EtOH}$ 2460, 2840 Å, $\varepsilon\varepsilon_{max}$ 8900, 3150.

The orange-brown *mono*-2:4-*dinitrophenylhydrazone* had m.p. 197–199° (from dioxane) (Found: C, 62·70; H, 5·40. $C_{22}H_{22}O_5N_4$ requires C, 62·55; H, 5·25%). The infra-red spectrum showed that the alicyclic carbonyl group was free (band at 1705 cm^{-1}). Ultra-violet absorption: λ_{max}^{chf} 3630 Å; ε_{max} 28,500.