622. *The Synthesis of 3 : 4-Benzofluorene and Some of its Monomethyl Derivatives.*

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Ethyl 4- and 5-methyl-1-β-naphthylmethyl-2-oxo*cyclo*hexanecarboxylate have been cyclised with good yields to ethyl 6 : 7 : 8 : 13-tetrahydro-6- and -7-methyl-3 : 4-benzofluorene-13-carboxylate respectively. These were dehydrogenated to the methyl-3 : 4-benzofluorenes. 2-β-Naphthylmethyl- and 3-methyl-2-β-naphthylmethyl-*cyclo*hexanone likewise gave 5 : 6 : 7 : 8-tetrahydro- and 5 : 6 : 7 : 8-tetrahydro-8-methyl-3 : 4-benzofluorene, and thence 3 : 4-benzofluorene and 8-methyl-3 : 4-benzofluorene. 5-Methyl-3 : 4-benzofluorene could not be obtained by either method.

Orchin and Friedel [1] commented on certain characteristics of 3 : 4-benzofluorene and suggested that strain is caused by hydrogen overlap between positions 4′ and 5. Such strain would obviously be increased by the substitution of methyl groups at these positions, and would become considerable in naphtho(2′ : 1′-3 : 4)fluorene (I) and its homologues. The two series of compounds would represent limiting cases of molecular overcrowding studied by Newman and Wheatley [2] in the 3 : 4-benzophenanthrene group.

Accordingly, we sought to develop a synthesis of methyl-3 : 4-benzofluorenes which would provide in the first instance 5-methyl-3 : 4-benzofluorene and would be applicable to the naphtho(2′ : 1′-3 : 4)fluorenes. Only 6-,[3,4] 8-,[4,5] and 9-methyl-3 : 4-benzofluorene [6] have been described hitherto, and the methods used for the first two of these were not satisfactory. The reactions described in this paper provided satisfactory routes to 6-, 7-, and 8-methyl-3 : 4-benzofluorene, but failed for the required 5-isomer. A good synthesis of the last-named compound will be described shortly.

Bougault-type [7] cyclisations have not often been used to construct five-membered rings.[8] Colonge and Sibeud [8c] claimed good yields of tetrahydrofluorenes by treating 2-benzyl*cyclo*hexanones with aluminium chloride or with hydrobromic–acetic acid, but Cook *et al.*[8a] obtained 3 : 4-benzofluorene (directly) in only 7·1% yield by boiling ethyl 1-β-naphthylmethyl-2-oxo*cyclo*hexanecarboxylate (II; R = R′ = R″ = R‴ = H) with 50% sulphuric acid. Catalytic dehydrogenation of the crude product did not significantly alter the yield.

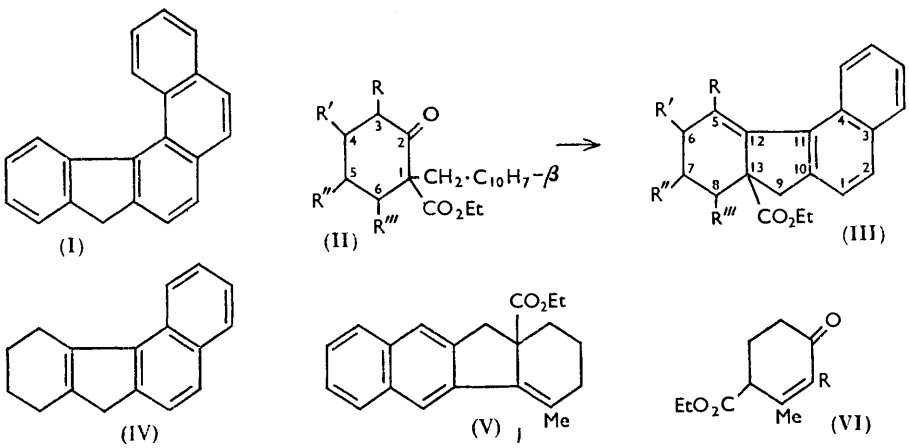
We re-examined the cyclisation of this ester (II; R = R′ = R″ = R‴ = H). Hydrogen fluoride left it unchanged or converted it into tars, depending on the time of contact. Modification of the original conditions [8a] by adding acetic acid to produce homogeneity did not improve the yield of 3 : 4-benzofluorene. Concentrated sulphuric acid at 0° gave only sulphonated derivatives, and polyphosphoric acid gave no recognisable product. However, when stirred for a short time at 0° with concentrated sulphuric acid and benzene, the ester gave a high yield of ethyl 6 : 7 : 8 : 13-tetrahydro-3 : 4-benzofluorene-13-carboxylate (III; R = R′ = R″ = R‴ = H), which formed a stable orange picrate. Prompted by this success, we examined the cyclisation of 2-β-naphthylmethyl-*cyclo*hexanone. This ketone was prepared by submitting benzyl 1-β-naphthylmethyl-2-oxo-*cyclo*hexanecarboxylate, obtained from the potassium derivative of benzyl 2-oxo*cyclo*-hexanecarboxylate [9] and 2-bromomethylnaphthalene, to catalytic debenzylation With

[1] Orchin and Friedel, *J. Amer. Chem. Soc.*, 1949, **71**, 3002.
[2] Newman and Wheatley, *ibid.*, 1948, **70**, 1913.
[3] Bachmann and Deno, *ibid.*, 1949, **71**, 3062.
[4] Harrill, Ph.D. Thesis, 1953, Northwestern University.
[5] Rapson and Shuttleworth, *J.*, 1940, 636.
[6] Fieser and Joshel, *J. Amer. Chem. Soc.*, 1940, **62**, 957.
[7] Cf. Linstead, *Ann. Reports*, 1936, **33**, 331.
[8] (*a*) Cook, Dansi, Hewett, Iball, Mayneord, and Roe, *J.*, 1935, 1319; (*b*) G.P. 725,278; (*c*) Colonge and Sibeud, *Bull. Soc. chim. France*, 1953, 75.
[9] Plieniger and Casto, *Chem. Ber.*, 1954, **87**, 1760.

benzene and sulphuric acid 2-β-naphthylmethyl*cyclo*hexanone gave a moderately good yield of 5 : 6 : 7 : 8-tetrahydro-3 : 4-benzofluorene (IV; position of double bond assumed) characterised as the chocolate-brown picrate.

These reactions opened the way to the synthesis of the methyl homologues. The potassio-derivatives of ethyl 3-, 4-, and 5-methyl-2-oxo*cyclo*hexanecarboxylate were readily converted into the methyl-1-β-naphthylmethyl-2-oxo*cyclo*hexanecarboxylates (II; R‴ = H; R″, R′, and R = Me or H). The second and third of these cyclised smoothly, giving the tetrahydro-compounds (III; R = R‴ = H; R″ and R′ = Me or H). Like the parent (III; R = R′ = R″ = R‴ = H) these gave orange picrates, but recrystallisation of ethyl 6 : 7 : 8 : 13-tetrahydro-6-methyl-3 : 4-benzofluorene-13-carboxylate picrate produced a dark-red hemi-picrate.

In contrast to the 4- and the 5-isomer, ethyl 3-methyl-1-β-naphthylmethyl-2-oxo*cyclo*hexanecarboxylate could not be cyclised to a structure of type (III) by any of the usual reagents. Sulphuric acid and benzene, acting for double the usual time, gave a poor yield of a product isomeric with the starting material. This substance did not form a picrate and gave no recognisable product upon catalytic dehydrogenation. It seems possible that it is a hydrate of the product of linear cyclisation (V). Such cyclisation in closely related cases was recently observed by Bendas and Djerassi,[10] and the difficulty of angular cyclisation recalls a number of other cases [11] in which steric factors are important. Prolonged acid hydrolysis of this ester (II; R = Me, R′ = R″ = R‴ = H) gave 6-methyl-2-β-naphthylmethyl*cyclo*hexanone, but this could not be cyclised under any of the conditions examined.



Ethyl 6-methyl-2-oxo*cyclo*hexanecarboxylate [12] is not readily available. Accordingly, we prepared ethyl 2-methyl-3-β-naphthylmethyl-4-oxo*cyclo*hex-2-enecarboxylate from Hagemann's ester (VI; R = H). Attempts to aralkylate the potassio-derivative of (VI) with 2-bromomethylnaphthalene in benzene–dimethylformamide [13] appeared to cause extensive decomposition of the dimethylformamide (despite careful purification of this solvent). With the sodio-derivative of (VI) less decomposition occurred but the yield of the desired product was very poor. Finally, ethyl 2-methyl-3-β-naphthylmethyl-4-oxo-*cyclo*hex-2-enecarboxylate (VI; R = CH_2·$C_{10}H_7$-β) was prepared satisfactorily from the sodio-derivative of (VI; R = H), obtained from sodamide in liquid ammonia,[14] and 2-bromomethylnaphthalene in toluene–ether. Alkaline hydrolysis of the product gave

[10] Bendas and Djerassi, *J. Amer. Chem. Soc.*, 1956, **78**, 2474.
[11] Cook, *Ann. Reports*, 1942, **39**, 171.
[12] Mukherjee and Bhattacharyya, *J. Indian Chem. Soc.*, 1946, **23**, 451.
[13] Stork and Burgstahler, *J. Amer. Chem. Soc.*, 1951, **73**, 3544.
[14] Hogg, *ibid.*, 1948, **70**, 161.

non-ketonic material, but acid hydrolysis provided 3-methyl-2-β-naphthylmethyl*cyclo*hex-2-enone, which could be readily hydrogenated to 3-methyl-2-β-naphthylmethyl*cyclo*hexanone. In the usual way the latter provided a moderately good yield of 5 : 6 : 7 : 8-tetrahydro-8-methyl-3 : 4-benzofluorene, characterised as its chocolate-brown picrate which was almost identical in appearance with the lower homologue mentioned above.

The various tetrahydro-3 : 4-benzofluorenes so prepared were dehydrogenated to 3 : 4-benzofluorene and its 6-, 7-, and 8-methyl derivatives. The temperature and time of dehydrogenation needed careful moderation, and on the larger scale the reaction was best effected in boiling diphenyl. The four aromatic hydrocarbons were characterised by conversion into their red picrates and bright-orange trinitrobenzene complexes. The m. p.s of the derivatives of 6-methyl-3 : 4-benzofluorene differ substantially from those reported by Bachmann and Deno.[3] Orchin and Friedel [1] commented on the stability of 3 : 4-benzofluorene picrate when compared with the dipicrates of 1 : 2- and 2 : 3-benzofluorene. We noticed, however, that 3 : 4-benzofluorene picrate, and more especially 7- and 8-methyl-3 : 4-benzofluorene picrate, decomposed appreciably—in the case of the 7-isomer rapidly enough to make accurate analysis difficult—when kept in air at room temperature. The trinitrobenzene complexes were stable.

A promising approach to 8-substituted 3 : 4-benzofluorenes failed because we could not satisfactorily combine the potassio-derivative of dihydroresorcinol dimethyl ether with 2-bromomethylnaphthalene. Even with a large excess of the second reagent, reaction in liquid ammonia gave back most of the dihydroresorcinol dimethyl ether unchanged. Hydrolysis of the crude reaction product provided a very low yield of 2-β-naphthylmethyl-*cyclo*hexane-1 : 3-dione.

Rapson and Shuttleworth [5] obtained 3 : 4-benzofluorene and 8-methyl-3 : 4-benzofluorene in very poor yields by treating 2-benzylidene- and 2-*o*-tolylidene-α-tetralone with phosphoric anhydride in boiling xylene. Our own experiments, and those of Colonge and Sibeud,[8c] prompted us to examine a modification of this synthesis using 2-benzyl-α-tetralone. The latter was best prepared by hydrogenation of the benzylidene compound. The methods of Colonge and Sibeud [8c] left 2-benzyl-α-tetralone unchanged, and benzene–sulphuric acid caused sulphonation, but phosphoric anhydride in boiling xylene gave, in poor yield, a mixture of three products. These were an oily hydro-3 : 4-benzofluorene (the analysis of which corresponded to a hexa- rather than the expected di-hydro-compound) and two solids, m. p.s 105° and 185°, severally. The oil readily gave 3 : 4-benzofluorene when dehydrogenated. The lower-melting solid was obtained in amounts insufficient even for analysis, but the compound, m. p. 185°, proved to be isomeric with 3 : 4-benzofluorene. Direct comparisons were not made, but it is striking that 1 : 2-benzofluorene is reported [15] to melt at 188° or 184°, and migration of the benzyl group may well have occurred.

Experimental

Ethyl 5- (b. p. 117—120°/14—15 mm.; 40%), 4- (b. p. 118—120°/14 mm.; 44%) and 3-methyl-2-oxo*cyclo*hexanecarboxylate (b. p. 110—111°/10 mm.; 52%) were prepared substantially by the same method as ethyl 2-oxo*cyclo*hexanecarboxylate.[16] 2-Bromomethylnaphthalene was obtained from 2-methylnaphthalene and *N*-bromosuccinimide, or by photobromination.[17] The former method gave 40—45% of product but was not satisfactory on the large scale; the second method gave 30—40% yield on any scale, and the remainder of the starting material was recovered. Rapid distillation of the unstable bromomethyl compound gave material sufficiently pure for use.

Ethyl 1-β-*Naphthylmethyl*-2-*oxo*cyclo*hexanecarboxylate*.—By the method of Cook *et al.*[8a] ethyl 2-oxo*cyclo*hexanecarboxylate (24·0 g.) gave ethyl 1-β-naphthylmethyl-2-oxo*cyclo*hexanecarboxylate (29·6 g.), b. p. 180—190°/0·2 mm., prisms, m. p. 69—71° [from light petroleum (b. p. 40—60°)].

[15] Graebe, *Annalen*, 1904, **335**, 134; Cook, *J.*, 1934, 374.
[16] *Org. Synth.*, Coll. Vol. II, p. 531.
[17] Chapman and Williams, *J.*, 1952, 5044.

In the same way were obtained *ethyl* 5- [64%; b. p. 200—204°/0·4 mm., prisms, m. p. 77—78° (Found: C, 78·8; H, 7·4. $C_{21}H_{24}O_3$ requires C, 77·75; H, 7·5%)], 4- [52%; needles, m. p. 70—71° (Found: C, 78·6; H, 7·5%)], and 3-*methyl*-1-β-*naphthylmethyl*-2-*oxo*cyclo*hexanecarboxylate* [60%; b. p. 180—190°/0·1 mm., prisms, m. p. 107—108° (Found: C, 77·6; H, 7·3%)]. *Benzyl* 1-β-*naphthylmethyl*-2-*oxo*cyclo*hexanecarboxylate* crystallised without distillation and from light petroleum (b. p. 40—60°) formed quilted needles, m. p. 75—76° (Found: C, 80·9; H, 6·45. $C_{25}H_{24}O_3$ requires C, 80·6; H, 6·5%); the *semicarbazone* gave needles, m. p. 204—205° (Found: C, 72·75; H, 6·3. $C_{26}H_{27}O_3N_3$ requires C, 72·7; H, 6·3%), from the same solvent.

2-β-*Naphthylmethyl*cyclo*hexanone*.—(*a*) When the foregoing benzyl ester (1·0 g.), 30% palladised charcoal (0·4 g.), and ethanol were shaken with hydrogen, reaction stopped after rapid uptake of 40 c.c. Filtration, addition of fresh catalyst (0·1 g.), and renewed hydrogenation completed the reaction. Filtration and removal of the solvent gave an oil (0·57 g.) which crystallised. 2-β-*Naphthylmethyl*cyclo*hexanone* gave needles, m. p. 58—60° (Found: C, 85·3; H, 7·6. $C_{17}H_{18}O$ requires C, 85·7; H, 7·6%), from aqueous methanol.

(*b*) Catalyst poisoning was not observed when the ester (4·0 g.), ethyl acetate (100 c.c.), and 20% palladised strontium carbonate [18] (1·0 g.) were shaken with hydrogen. After removal of the catalyst the solution was refluxed for ½ hr. and evaporated, giving the product (1·76 g.). The *semicarbazone* separated from ethanol as needles, m. p. 179—181° (Found: C, 73·0; H, 7·1. $C_{18}H_{21}ON_3$ requires C, 73·2; H, 7·2%). The *picrate* formed yellow needles, m. p. 84—85° (Found: C, 59·0; H, 4·5. $C_{23}H_{21}O_8N_3$ requires C, 59·1; H, 4·5%), from the same solvent.

Ethyl 2-*Methyl*-3-β-*naphthylmethyl*-4-*oxo*cyclo*hex*-2-*enecarboxylate*.—Ethyl 2-methyl-4-oxo-*cyclo*hex-2-enecarboxylate [14] (30·3 g.) was added all at once to a stirred suspension of sodamide [prepared from sodium (3·88 g.) and liquid ammonia (100 c.c.)] cooled in carbon dioxide–acetone. The mixture was stirred for 20 min. without cooling, then cooled again, and treated with a mixture of dry toluene (100 c.c.) and ether (17 c.c.). The mixture was stirred without cooling for 1½ hr., most of the ammonia evaporating. 2-Bromomethylnaphthalene (36·9 g.) in toluene (150 c.c.) was then added in a steady stream, and the mixture was refluxed for 18 hr. under nitrogen. After addition of water the organic layer was washed with dilute hydrochloric acid and water and dried (Na_2SO_4). Evaporation and distillation gave a pale yellow oil (28·0 g.), b. p. 210—220°/0·2 mm. The *semicarbazone* formed prisms, m. p. 188—189° (Found: C, 67·85; H, 7·1. $C_{22}H_{25}O_3N_3,\frac{1}{2}C_2H_5{\cdot}OH$ requires C, 67·7; H, 7·3%), from ethanol.

3-*Methyl*-2-β-*naphthylmethyl*cyclo*hex*-2-*enone*.—The above oil (28·0 g.), acetic acid (1120 c.c.), and 2N-hydrochloric acid (560 c.c.) were refluxed under nitrogen for 6 hr. The benzene extract of the diluted solution was washed with sodium carbonate solution and with water, dried, and evaporated. The ketone (13·2 g.) was obtained as a pale yellow oil, b. p. 170—174°/0·05 mm. The *semicarbazone* crystallised from ethanol as needles, m. p. 190—191° (Found: C, 74·0; H, 7·0. $C_{19}H_{21}ON_3$ requires C, 74·2; H, 6·9%).

3-*Methyl*-2-β-*naphthylmethyl*cyclo*hexanone*.—The above ketone (5·0 g.), Adams platinum oxide catalyst (0·75 g.) and ethanol (80 c.c.) were shaken with hydrogen. When uptake ceased (680 ml.) the mixture was filtered, evaporated, and distilled. The ketone (4·0 g.) had b. p. 160—166°/0·05 mm. The *semicarbazone* gave needles, m. p. 207—208° (Found: C, 74·1; H, 7·8. $C_{19}H_{23}ON_3$ requires C, 73·75; H, 7·5%), from ethanol.

2-*Methyl*-6-β-*naphthylmethyl*cyclo*hexanone*.—Ethyl 3-methyl-1-β-naphthylmethyl-2-oxo-*cyclo*hexanecarboxylate (3·4 g.), acetic acid (120 c.c.), and 2N-hydrochloric acid (60 c.c.) were heated under reflux for 60 hr. Working up in the usual way with ether yielded a crude product (1·0 g.), m. p. 65—70°, after trituration with light petroleum (b. p. 40—60°). The *ketone* gave from this solvent needles, m. p. 73—74° (Found: C, 85·3; H, 8·0. $C_{18}H_{20}O$ requires C, 85·7; H, 8·0%).

Ethyl 6 : 7 : 8 : 13-*Tetrahydro*-3 : 4-*benzofluorene*-13-*carboxylate*.—Ethyl 1-β-naphthylmethyl-2-oxo*cyclo*hexanecarboxylate (5·0 g.) and benzene (100 c.c.) were stirred vigorously at 0° and treated dropwise during 20 min. with ice-cold concentrated sulphuric acid (60 c.c.). The deep-red solution was stirred at 0° for a further 70 min. and poured on ice. The benzene extract from the mixture was washed with dilute sodium carbonate solution and with water. The dried (Na_2SO_4) extract gave an oil (3·6 g.), which on distillation (b. p. 160—162°/0·02 mm.) was pale yellow (2·2 g.). From aqueous ethanol the *tetrahydro-compound* formed needles, m. p. 65—66° (Found: C, 81·9; H, 7·0. $C_{20}H_{20}O_2$ requires C, 82·15; H, 6·9%). The *picrate* gave orange

[18] Bowman, *J.*, 1950, 325.

needles, m. p. 114—115° (Found : C, 59·8; H, 4·7. $C_{26}H_{23}O_9N_3$ requires C, 59·9; H, 4·45%), from ethanol.

Ethyl 6 : 7 : 8 : 13-*Tetrahydro*-7-*methyl*-3 : 4-*benzofluorene*-13-*carboxylate*.—Prepared in the manner described above (50—63% yield) as a pale yellow oil, b. p. 167—170°/0·02 mm., the *tetrahydro-compound* formed prisms, m. p. 57—58° (Found : C, 82·0; H, 6·9. $C_{21}H_{22}O_2$ requires C, 82·3; H, 7·2%), from aqueous methanol. The *picrate* gave orange needles, m. p. 104—105° (Found : C, 61·0; H, 4·9. $C_{21}H_{22}O_2,C_6H_3O_7N_3$ requires C, 60·6; H, 4·7%), from ethanol.

Ethyl 6 : 7 : 8 : 13-*Tetrahydro*-6-*methyl*-3 : 4-*benzofluorene*-13-*carboxylate*.—The pale yellow oil (68%), b. p. 162—166°/0·05 mm., gave prisms of the *tetrahydro-compound*, m. p. 78—79° (Found : C, 81·4; H, 6·7%), from aqueous methanol. From ethanol the *hemipicrate* formed red platelets, m. p. 107—108° (Found : C, 67·85; H, 5·8. $C_{21}H_{22}O_2,\frac{1}{2}C_6H_3O_7N_3$ requires C, 68·5; H, 5·6%).

5 : 6 : 7 : 8-*Tetrahydro*-3 : 4-*benzofluorene*.—A vigorously stirred solution of 2-β-naphthylmethyl*cyclo*hexanone (0·5 g.) in benzene (5 ml.) was treated at 0°, during 10 min., with ice-cold concentrated sulphuric acid. The deep-red solution was stirred for 80 min. more at 0° and worked up in the usual way. The crude oil (0·36 g.), when triturated with light petroleum (b. p. 40—60°), gave a solid (0·25 g.), m. p. 85—90°. 5 : 6 : 7 : 8-*Tetrahydro*-3 : 4-*benzofluorene*, m. p. 95—96° (Found : C, 92·9; H, 6·8. $C_{17}H_{16}$ requires C, 92·7; H, 7·3%), crystallised from aqueous ethanol. Chocolate-brown needles of the *picrate*, m. p. 129—130° (Found : C, 61·5; H, 4·1. $C_{23}H_{19}O_7N_3$ requires C, 61·5; H, 4·3%), separated from ethanol.

5 : 6 : 7 : 8-*Tetrahydro*-8-*methyl*-3 : 4-*benzofluorene*.—Prepared as above (47%) the 8-*methyl compound* gave plates, m. p. 52—53° (Found : C, 91·0; H, 7·5. $C_{18}H_{18}$ requires C, 92·3; H, 7·7%), from aqueous ethanol. The chocolate-brown *picrate* gave needles, m. p. 125—126° (Found : C, 62·3; H, 4·6. $C_{24}H_{21}O_7N_3$ requires C, 62·2; H, 4·6%), from ethanol.

Attempted Cyclisation of Ethyl 3-*Methyl*-1-β-*naphthylmethyl*-2-*oxo*cyclo*hexanecarboxylate*.—Treated in the way described above, this substance remained unchanged; a reaction time of 6 hr. caused complete sulphonation. After 3 hr. a very small yield of a *substance* was isolated which gave needles, m. p. 79—80° (Found : C, 77·0; H, 7·6. $C_{21}H_{24}O_3$ requires C, 77·75; H, 7·5%), from aqueous methanol.

3 : 4-*Benzofluorene*.—(*a*) Ethyl 6 : 7 : 8 : 13-tetrahydro-3 : 4-benzofluorene-13-carboxylate (1·0 g.) and 30% palladised charcoal (0·5 g.) were heated under nitrogen for 4 hr. at 280°. Sublimation at 120°/0·1 mm. gave 3 : 4-benzofluorene (0·46 g.), m. p. 110—115° (m. p., after crystallisation from ethanol, 122—124°; picrate, m. p. 130—131°). 5 : 6 : 7 : 8-Tetrahydro-3 : 4-benzofluorene (0·40 g.) in the same way (240°, 1¾ hr.) gave the product (0·15 g.).

(*b*) 2-Benzyl-α-tetralone (9·68 g.), phosphoric anhydride (10 g.), and xylene (100 c.c.) were heated under reflux for 12 hr., more phosphoric anhydride (10 g.) being added after 6 hr. The xylene solution was decanted, the solid residue was decomposed with ice and extracted with benzene, and the benzene and xylene solutions were combined, washed with dilute alkali and water, and dried. Distillation gave a clear mobile oil (2·66 g.), b. p. 120—130°/0·05 mm., and a viscous yellow oil (0·4 g.), b. p. 160—170°/0·1 mm., which immediately crystallised.

Redistillation of the mobile oil gave *hexa*(?)*hydro*-3 : 4-*benzofluorene*, b. p. 120—122°/0·02 mm. (n_D^{17} 1·6095) (Found : C, 91·8; H, 8·0. $C_{17}H_{18}$ requires C, 91·8; H, 8·2%). This (0·5 g.) with 30% palladised charcoal (0·1 g.) for 1½ hr. at 220—240° gave by ether-extraction a brown oil (0·46 g.) which immediately crystallised. With picric acid in ethanol this gave 3 : 4-benzofluorene picrate, m. p. and mixed m. p. 130—131°.

Fractional crystallisation from ethanol of the solid material from the distillation gave small quantities of two substances : white flakes, m. p. 184—185° (Found : C, 94·3; H, 5·7. Calc. for $C_{17}H_{12}$: C, 94·4; H, 5·6%) (1 : 2-benzofluorene is reported [15] to have m. p. 188° and 184°), and prisms, m. p. 104—105° (insufficient for analysis).

6-*Methyl*-3 : 4-*benzofluorene*.—Ethyl 4-methyl-1-β-naphthylmethyl-2-oxo*cyclo*hexanecarboxylate (2·2 g.), diphenyl (5·0 g.), and 30% palladised charcoal (0·6 g.) were heated under nitrogen at 260° for 3½ hr. The ether was removed from a filtered ether extract of the product, and most of the diphenyl was removed by distillation under reduced pressure. The residue was treated in ethanol with an equal weight of picric acid, giving a bright red picrate (1·4 g.), m. p. 139—141° [needles from ethanol, m. p. 141—142° (Found : C, 62·7; H, 3·7. Calc. for $C_{18}H_{14},C_6H_3O_7N_3$: C, 62·7; H, 3·7%)]. The hydrocarbon regenerated by lithium hydroxide (0·7 g.) gave flakes of 6-methyl-3 : 4-benzofluorene, m. p. 76—77°, from ethanol. The trinitrobenzene complex formed yellowish-orange needles, m. p. 159—160°, from ethanol.

Bachmann and Deno [3] gave m. p.s 72—72·5°, 119—120·5°, and 147·5—148·5°, for the hydrocarbon, picrate, and trinitrobenzene complex, respectively.

7-*Methyl*-3 : 4-*benzofluorene*.—Prepared as above from the appropriate tetrahydro-ester (3·75 g.), 7-*methyl*-3 : 4-*benzofluorene* (crude yield 1·29 g.; m. p. 77—80°) gave needles, m. p. 79—80° (Found : C, 93·7; H, 6·0. $C_{18}H_{14}$ requires C, 93·9; H, 6·1%), from aqueous ethanol. The red needles, m. p. 136—137°, of the picrate (from ethanol) dissociated fairly quickly in the air and did not give accurate analyses (Found : C, 64·15; H, 3·7%). The *trinitrobenzene complex*, yellow-orange needles (from ethanol), m. p. 146—147° (Found : C, 65·1; H, 3·9. $C_{18}H_{14},C_6H_3O_6N_3$ requires C, 65·0; H, 3·9%), was stable.

8-*Methyl*-3 : 4-*benzofluorene*.—5 : 6 : 7 : 8-Tetrahydro-8-methyl-3 : 4-benzofluorene (0·4 g.), heated with palladised charcoal at 180—240° during 1½ hr., gave the substantially pure product (0·21 g.). It formed flakes, m. p. 107—108°, from ethanol [picrate (bright-red needles), m. p. 129—130°, from ethanol]. The *trinitrobenzene complex* gave orange-needles, m. p. 164—165° (Found : C, 64·4; H, 3·8%), from ethanol.

2-β-*Naphthylmethyl*cyclo*hexane*-1 : 3-*dione*.—1 : 5-Dimethoxy*cyclo*hexa-1 : 4-diene (42 g.) was added during 15 min. to a potassamide solution [from potassium (12 g.) and liquid ammonia (600 c.c.)]. The deep-red solution was stirred for 20 min. more, and treated dropwise with 2-bromomethylnaphthalene in ether until the red colour was completely discharged. Decomposition with ice and water, extraction with ether, removal of the ether, and distillation of excess of dimethoxy*cyclo*hexa-1 : 4-diene left an oil (7·1 g.). This was boiled with 2N-sulphuric acid (30 c.c.) for 1 hr. Extraction of the mixture with ether, and of the ether with dilute sodium hydroxide solution followed by acidification of the alkaline solution, gave the product (0·7 g.). 2-β-*Naphthylmethyl*cyclo*hexane*-1 : 3-*dione* gave plates, m. p. 205—206° (Found : C, 80·9; H, 6·2. $C_{17}H_{16}O_2$ requires C, 80·9; H, 6·4%), from ethyl acetate.

2-*Benzyl*-α-*tetralone*.—2-Benzylidene-α-tetralone [5] (13·4 g.), purified dioxan (215 c.c.), and 10% palladised strontium carbonate (1·34 g.) were shaken with hydrogen until the calculated quantity of the latter was consumed. The usual methods gave 2-benzyl-α-tetralone as a pale-yellow oil, b. p. 148—150°/0·05 mm., which crystallised immediately (m. p. 45—49°) and gave an oxime, m. p. 121—122°.

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