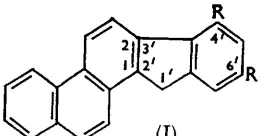
780. *Synthesis of Polycyclic Compounds. Part VII.* A Shorter Route to Indeno(2′,3′-1,2)phenanthrene and its Analogues.*

By B. B. Datta and J. C. Bardhan.

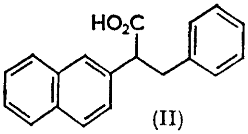
Aromatic aldehydes react with arylacetic acids and the products on reduction and cyclisation afford 2-arylindanones. The latter on Reformatsky reaction, dehydration, and hydrolysis furnish substituted indenylacetic acids. These on further ring closure, reduction, and dehydrogenation lead to benzofluorenes and indenophenanthrenes. Four hydrocarbons have been synthesised in good yields by this general method.

Several methods are on record for the synthesis of indeno(2′,3′-1,2)phenanthrene (I; R = R′ = H) and its derivatives,[1] but their applicability is very limited. The following method is more general and gives good yields.

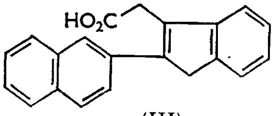
Benzaldehyde and 2-naphthylacetic acid in presence of acetic anhydride–triethylamine[2] give an unsaturated acid which was reduced with sodium amalgam to the propionic acid (II). The latter smoothly underwent intramolecular Friedel–Crafts acylation[3] with the formation of the ketone which, on reaction with ethyl bromoacetate and zinc, dehydration, and hydrolysis, gave the substituted indenylacetic acid (III). This was cyclised by phosphorus pentachloride and stannic chloride,[4] and the ketone obtained was reduced by Huang-Minlon modification of the Wolff–Kishner method, and the product (IV) was dehydrogenated with selenium to give the indenophenanthrene (I; R = R′ = H).



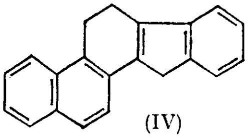
(I)



(II)



(III)



(IV)

The same reactions with 3,5-dimethylbenzaldehyde led to the 4′,6′-dimethyl derivative (I; R = R′ = Me).

2-Phenylindan-1-one and its 6,7-benzo-derivative were obtained analogously and converted into 1,2-benzo- and 1,2:5,6-dibenzo-fluorene, respectively.

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* Part VI, *J.*, 1956, 4629.

[1] Bamberger and Chattaway, *Annalen*, 1895, **284**, 52; Cook, *J.*, 1941, 685; Cook, Hewett, Mayneord, and Roe, *J.*, 1934, 1728; Nasipuri and Roy, *J.*, 1961, 3362.

[2] Cf. Buckles and Hausman, *J. Amer. Chem. Soc.*, 1948, **70**, 415; *Org. Synth.*, 1955, **35**, 89.

[3] Thiele and Wanscheidt, *Annalen*, 1910, **376**, 269; Auwers and Auffenberg, *Ber.*, 1919, **52**, 108.

[4] Cf. Johnson, " Organic Reactions," John Wiley, New York, 1944, Vol. II, p. 136.

EXPERIMENTAL

α-2-*Naphthylcinnamic Acid.*—Benzaldehyde (12·7 g.), 2-naphthylacetic acid (32·4 g.), acetic anhydride (60 c.c.), and triethylamine (12·1 g.) were refluxed on a sand-bath for 20 min. The resulting solution was cooled to 90° and water (60 c.c.) was gradually added without allowing the temperature to fall. On cooling to 20°, crystals separated; these were collected, washed successively with 50% acetic acid (30 c.c.) and water, and dried. α-2-*Naphthylcinnamic acid* crystallised from toluene in almost colourless prisms, m. p. 188° (22·4 g.) (Found: C, 83·0; H, 5·0. $C_{19}H_{14}O_2$ requires C, 83·2; H, 5·1%).

α-2-*Naphthyl*-β-*phenylpropionic Acid* (II).—The preceding acid (22 g.) in N-sodium hydroxide (100 c.c.) was reduced with 2·5% sodium amalgam (240 g.) in the usual way. The product separated as an oil that solidified on storage. From light petroleum (b. p. 60—80°), the *propionic acid* formed needles, m. p. 147° (19 g.) (Found: C, 82·3; H, 5·6. $C_{19}H_{16}O_2$ requires C, 82·6; H, 5·8%).

2-2′-*Naphthylindan*-1-*one*.[3]—The propionic acid (11 g.) and thionyl chloride (4 c.c.) were kept at room temperature for 15 min., then at 50—60° for 2 hr. The excess of thionyl chloride was removed under reduced pressure and the residue mixed with light petroleum (50 c.c.; b. p. 60—80°). Powdered aluminium chloride (9 g.) was introduced in three portions with shaking. The mixture was refluxed for 2 hr. and, on cooling, was decomposed with ice and hydrochloric acid, and the product was extracted with benzene. 2-2′-*Naphthylindan*-1-*one* (5 g.) crystallised from acetic acid and had m. p. 120° (Found: C, 88·1; C, 5·4. $C_{19}H_{14}O$ requires C, 88·4; H, 5·4%). The *semicarbazone* formed prisms, m. p. 182°, from alcohol (Found: C, 76·0; H, 5·3. $C_{20}H_{17}N_3O$ requires C, 76·2; H, 5·4%).

2-2′-*Naphthylinden*-3-*ylacetic Acid* (III).—The preceding ketone (4·5 g.), zinc turnings (10·5 g.), iodine (0·5 g.), ethyl bromoacetate (3·5 c.c.), redistilled benzene (44 c.c.), and dry ether (44 c.c.) were gently refluxed [5] on the water-bath for 6 hr. The product was cooled and poured into an excess of ice-cold dilute hydrochloric acid. The organic layer was separated, the aqueous phase was extracted with ether, and the combined extracts were washed, dried ($MgSO_4$), and evaporated. The crude residue (5 g.) was heated with anhydrous formic acid (10·5 c.c.) on the steam-bath for 30 min. and the excess of formic acid removed. The unsaturated material (6 g.) was then boiled with potassium hydroxide (3·2 g.) in water (3 c.c.) and alcohol (12 c.c.) for 1 hr. The alcohol was removed on the water-bath, the residue cooled and extracted with chloroform, and the alkaline solution acidified with hydrochloric acid. 2-2′-*Naphthylinden*-3-*ylacetic acid* crystallised from acetic acid (charcoal) as needles (3·4 g.), m. p. 145° (Found: C, 83·7; H, 5·2. $C_{21}H_{16}O_2$ requires C, 84·0; H, 5·3%).

3,4-*Dihydro*-4-*oxoindeno*(3′,2′-1,2)*phenanthrene*.—The preceding acid (3 g.) was dissolved in dry benzene (10 c.c.) and finely powdered phosphorus pentachloride (2·3 g.) added with shaking. The mixture was kept at the room temperature for 1 hr., then heated on the steam-bath for 5 min. The product was cooled in a freezing mixture and a solution of stannic chloride (1·5 c.c.) in dry benzene (5 c.c.) added rapidly with shaking. The mixture was kept at 0° for 2 hr., and a deep brown complex that separated was decomposed with ice, hydrochloric acid, and a little ether. The solvent was removed in steam and the residue collected in chloroform, washed with dilute hydrochloric acid, water, a dilute solution of sodium hydroxide, and water, dried (Na_2SO_4), and recovered. This *ketone* (1·6 g.) crystallised from acetic acid (charcoal) as scales, m. p. 202° (Found: C, 89·0; H, 4·8. $C_{21}H_{14}O$ requires C, 89·3; H, 4·9%). The 2,4-*dinitrophenylhydrazone* formed brick-red prisms, m. p. 258° (decomp.), from alcohol (Found: C, 70·0; H, 3·8. $C_{27}H_{18}N_4O_4$ requires C, 70·1; H, 3·9%).

3,4-*Dihydroindeno*(3′,2′-1,2)*phenanthrene* (IV).—The last-mentioned ketone (1·3 g.), potassium hydroxide (1·2 g.), 80% hydrazine hydrate (1 c.c.), and ethylene glycol (10 c.c.) were heated at 160° under a water-separator for 1·5 hr.; the temperature was gradually raised to 195—200° and heating continued for 5 hr. more. Water (10 c.c.) was added and the mixture poured into ice-cold 6N-hydrochloric acid (30 c.c.). The solid which separated gave, on purification from benzene (charcoal), the *dihydro-compound* (IV) (0·95 g.) as plates, m. p. 187° (Found: C, 93·8; H, 5·8. $C_{21}H_{16}$ requires C, 94·0; H, 5·9%).

Indeno(3′,2′-1,2)*phenanthrene* (I; R = R′ = H).—The dihydro-derivative (0·6 g.) was heated with selenium (1·2 g.) at 300—320° for 20 hr. The mass was then powdered and digested

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[5] Bachman, *J. Org. Chem.*, 1938, 434.

with acetic acid, and the solution was filtered and evaporated. The residue, on recrystallisation from benzene (charcoal), gave the indenophenanthrene (0·35 g.) as plates, m. p. 335—336° (Found: C, 94·5; H, 5·1. Calc. for $C_{21}H_{14}$: C, 94·7; H, 5·2%). Cook *et al.*[1] report m. p. 335°. The fluorenone obtained on oxidation crystallised as orange red needles, m. p. 207°, from acetic acid (Cook *et al.*[1] give m. p. 207—208°).

4′,6′-*Dimethylindeno*(3′,2′-1,2)*phenanthrene* (I; R = R′ = Me).—3,5-Dimethylbenzyl bromide[6] was prepared by heating mesitylene (68 g.) with bromine (24 c.c.) at 135—145° for 6 hr., as described by Atkinson and Thorpe[7] for an analogous case. It (56 g.) had b. p. 112—115°/18 mm.

To this bromide (54 g.) in alcohol (210 c.c.), hexamine (40·4 g.) and water (41 c.c.) were added with shaking. The solution was diluted with water (168 c.c.) and refluxed for 2 hr. Hydrochloric acid (60 c.c.) was then added and refluxing continued for 5 min. more. 3,5-Dimethylbenzaldehyde (30 g.) was isolated by distillation in steam and had b. p. 110—112°/16 mm. (semicarbazone, m. p. 201°) (lit.,[8] b. p. 220—222°/760 mm.; m. p. 201·5°).

Under the various conditions described above, this aldehyde gave the following compounds (yields are for each stage): 3,5-*dimethyl*-α-2′-*naphthylcinnamic acid* (23 g. of aldehyde), needles (from toluene), m. p. 208° (Found: C, 83·1; H, 5·9. $C_{21}H_{18}O_2$ requires C, 83·4; H, 5·9%); β-3,5-*dimethylphenyl*-α-2′-*naphthylpropionic acid*, scales, m. p. 142° (from alcohol) (Found: C, 82·7; H, 6·4. $C_{21}H_{20}O_2$ requires C, 82·9; H, 6·6%); 5,7-*dimethyl*-2-2′-*naphthylindan*-1-*one*, needles (6·8 g. from 12·2 g.) (from alcohol; charcoal), m. p. 103° (Found: C, 87·8; H, 6·2. $C_{21}H_{18}O$ requires C, 88·1; H, 6·3%) [*semicarbazone*, m. p. 170° (from alcohol) (Found: C, 76·7; H, 6·0. $C_{22}H_{21}N_3O$ requires C, 76·9; H, 6·1%)]; 4,6-*dimethyl*-2-2′-*naphthylinden*-3-*yl-acetic acid* (3 g. from 4·8 g.), needles (from acetic acid; charcoal), m. p. 133° (Found: C, 83·8; H, 6·0. $C_{23}H_{20}O_2$ requires C, 84·1; H, 6·1%); 3,4-*dihydro*-4′,6′-*dimethyl*-4-*oxoindeno*(3′,2′-1,2)-*phenanthrene* (1·7 g. from 3·2 g.), needles (from acetic acid; charcoal), m. p. 193° (Found: C, 88·7; H, 5·7. $C_{23}H_{18}O$ requires C, 89·0; H, 5·8%) [2,4-*dinitrophenylhydrazone*, m. p. 221° (Found: C, 70·8; H, 4·4. $C_{29}H_{22}N_4O_4$ requires C, 71·0; H, 4·5%)]; 3,4-*dihydro*-4′,6′-*dimethylindeno*(3′,2′-1,2)*phenanthrene*, scales (from benzene, charcoal), m. p. 172° (Found: C, 92·9; H, 6·7. $C_{23}H_{20}$ requires C, 93·2; H, 6·8%); 4′,6′-*dimethylindeno*(3′,2′-1,2)*phenanthrene* (0·3 g. from 0·6 g.), leaflets (from alcohol, charcoal), m. p. 214° (Found: C, 93·6; H, 6·0. $C_{23}H_{18}$ requires C, 93·9; H, 6·1%), yielding on oxidation the *indenone* as yellow leaflets, m. p. 197—198° (from acetic acid) (Found: C, 89·5; H, 5·3. $C_{24}H_{16}O$ requires C, 89·6; H, 5·2%).

1,2-*Benzofluorene*.—α-Phenylcinnamic acid,[9] prepared by the action of triethylamine[5] on benzaldehyde and phenylacetic acid, had m. p. 172° (from toluene) (Found: C, 80·1; H, 5·2. Calc. for $C_{15}H_{12}O_2$: C, 80·3; H, 5·3%). The derived propionic acid[10] crystallised from light petroleum (b. p. 60—80°) in flakes, m. p. 98° (Found: C, 79·3; H, 6·1. Calc. for $C_{15}H_{14}O_2$: C, 79·6; H, 6·2%). 2-Phenylindan-1-one[3] was prepared by the general procedure described above, and on recrystallisation from boiling alcohol had m. p. 77—78 (lit.,[3] 77—78°) (Found: C, 86·2; H, 5·6. Calc. for $C_{15}H_{12}O$: C, 86·5; H, 5·8%) (semicarbazone, m. p. 168°). This led, by reactions as described above, to: 2-*phenylinden*-3-*ylacetic acid*, needles (from acetic acid), m. p. 108° (Found: C, 81·4; H, 5·5. $C_{17}H_{14}O_2$ requires C, 81·6; H, 5·6%); 3,4-*dihydro*-3-*oxo*-1,2-*benzofluorene*, prisms (from alcohol; charcoal), m. p. 157° (Found: C, 87·6; H, 5·0. $C_{17}H_{12}O$ requires C, 87·9; H, 5·2%) (2,4-dinitrophenylhydrazone, m. p. 202°); 3,4-*dihydro*-1,2-*benzofluorene*, scales (from benzene; charcoal), m. p. 142° (Found: C, 93·3; H, 6·3. $C_{17}H_{14}$ requires C, 93·5; H, 6·4%); 1,2-benzofluorene, plates (from acetic acid), m. p. 182° (Found: C, 94·2; H, 5·3. Calc. for $C_{17}H_{12}$: C, 94·4; H, 5·5%) (Cook *et al.*,[1] 182—183°; Lothrop and Goodwin,[11] 182°). The corresponding fluorenone forms dark orange needles, m. p. 132° (from alcohol) (lit.,[1, 11] 131—132°, 133°).

1,2,5,6-*Dibenzofluorene*.—β-2-*Naphthyl*-α-*phenylacrylic acid*, prepared from 2-naphthaldehyde (25 g.), phenylacetic acid (32 g.), triethylamine (16 g.), and acetic anhydride (80 c.c.), formed needles (25 g.), m. p. 198° (from toluene) (Found: C, 82·9; H, 5·1. $C_{19}H_{14}O_2$ requires

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[6] Wispek, *Ber.*, 1883, **16**, 1577.

[7] Atkinson and Thorpe, *J.*, 1907, 1698.

[8] Etard, *Compt. rend.*, 1885, **97**, 910.

[9] Müller, *Ber.*, 1893, **26**, 659.

[10] Mayer, *Ber.*, 1888, **21**, 1308; Wislicenus and Goldstein, *Ber.*, 1895, **28**, 818.

[11] Lothrop and Goodwin, *J. Amer. Chem. Soc.*, 1943, **65**, 363.

C, 83·2; H, 5·1%). This led, as above, to: β-2-*naphthyl-α-phenylpropionic acid*, plates (from alcohol; charcoal), m. p. 152° (Found: C, 82·4; H, 5·7. $C_{19}H_{16}O_2$ requires C, 82·6; H, 5·8%); 2-*phenyl*-4,5-*benzindan*-3-*one* (5·2 g. from 8·3 g.), needles (from alcohol), m. p. 128° (Found: C, 88·0; H, 5·3. $C_{19}H_{14}O$ requires C, 88·4; H, 5·4%) (semicarbazone, m. p. 214°); 2-*phenyl*-4,5-*benzinden*-3-*ylacetic acid* (3·2 g. from 4·5 g.), needles (from acetic acid), m. p. 165° (Found: C, 83·7; H, 5·2. $C_{21}H_{16}O_2$ requires C, 84·0; H, 5·3%); 3,4-*dihydro*-3-*oxo*-1,2:5,6-*dibenzofluorene* (1·6 g. from 3·0 g.), needles (from acetic acid; charcoal), m. p. 197° (Found: C, 88·9; H, 4·8. $C_{21}H_{14}O$ requires C, 89·3; H, 5·0%) (2,4-dinitrophenylhydrazone, m. p. 212°); 3,4-*dihydro*-1,2:5,6-*dibenzofluorene* (0·9 g. from 1·2 g.), scales (from benzene; charcoal), m. p. 158° (Found: C, 93·7; H, 5·8. $C_{21}H_{16}$ requires C, 94·0; H, 6·0%); 1,2:5,6-dibenzofluorene (0·34 g. from 0·6 g.), plates (from benzene; charcoal), m. p. 174° (Found: C, 94·4; H, 5·1. Calc. for $C_{21}H_{14}$: C, 94·7; H, 5·3%) (lit.,[12] 171—172°,[13] 174—175°). The derived fluorenone forms deep red scales, m. p. 164°, from ethyl acetate, as reported.[12,13]

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Department of Chemistry, University College of Science,
Calcutta, India.
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[12] Cook, Dansi, Hewett, Iball, Mayneord, and Roe, *J.*, 1935, 1319.

[13] Swain and Todd, *J.*, 1941, 674.