537. *Further Studies in the Cyclodehydration of Arylidene-α-tetralones.*

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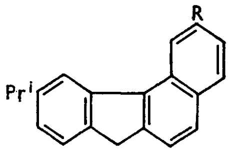
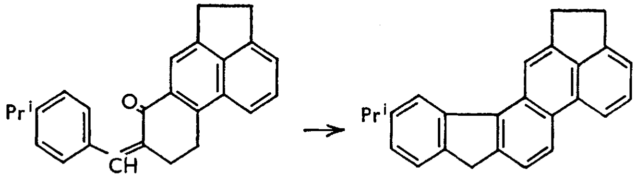
Cyclodehydration of arylidene-α-tetralones has been studied in respect of the preparation of new substituded 7*H*-benzo[*c*]fluorenes and of polycyclic hydrocarbons bearing two cyclopentadiene rings. Further, arylidene-α-tetralones derived from 2-quinolinaldehyde are shown to resist cyclodehydration.

2-BENZYLIDENE-1-TETRALONE was shown by Rapson and Shuttleworth [1] to undergo cyclodehydration with phosphorus pentoxide to give 7*H*-benzo[*c*]fluorene, and this reaction was later extended to the synthesis of a large number of more condensed polycyclic fluorene derivatives, some of which possess biological interest as carcinogens or as inhibitors of tumour-growth.[2] However, it had rarely been applied to the preparation of substituted 7*H*-benzo[*c*]fluorenes. The present work shows that cuminaldehyde can be used in such syntheses, 2-4′-isopropylbenzylidene-1-tetralone being readily converted into 10-isopropyl-7*H*-benzo[*c*]fluorene (I); 2-methyl-10-isopropyl-7*H*-benzo[*c*]fluorene (II) was similarly obtained. More condensed hydrocarbons with isopropyl groups were also prepared in



(I), R = H. (II), R = Me.



(III) (IV)

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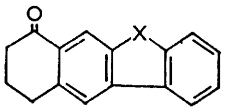
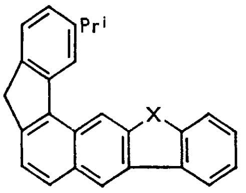
[1] Rapson and Shuttleworth, *J.*, 1940, 536; Buu-Hoï and Cagniant, *Rev. Sci.*, 1942, **80**, 319, 384, 436; 1943, **81**, 30; Buu-Hoï and Saint-Ruf, *J.*, 1957, 3806; Saint-Ruf, Buu-Hoï, and Jacquignon, *J.*, 1958, 48; 1959, 3237.

[2] Badger, Elson, Haddow, Hewett, and Robinson, *Proc. Roy. Soc.*, 1942, *B*, **130**, 255.

the same way; thus, cyclisation of the condensation product (III) of 4-isopropylbenzaldehyde with 7,8,9,10-tetrahydro-7-oxoacephenanthrene furnished the hydrocarbon (IV). Similar syntheses were also performed with tetralones bearing a furan or thiophen ring; the *p*-isopropylbenzylidene derivatives of ketones (V) and (VI), for instance, underwent ready condensation to compounds (VII) and (VIII).

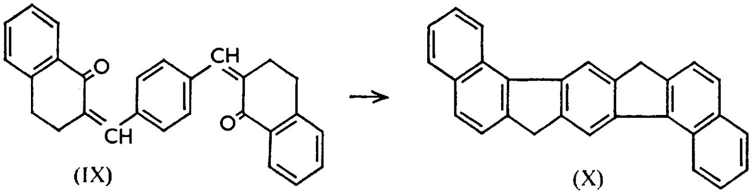
(V), X=O
(VI), X=S





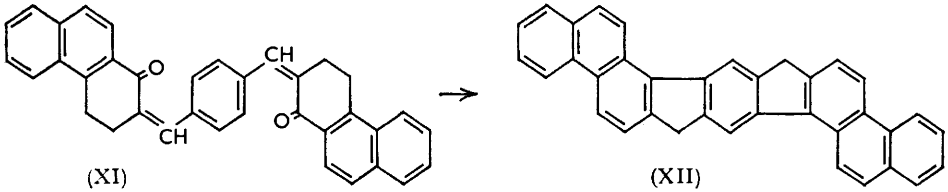
(VII), X=O
(VIII), X=S

The alkali-catalysed reaction of terephthalaldehyde with two mols. of α-tetralone involved both the aldehyde groups, to give the chalcone-like compound (IX); this was cyclised with phosphorus pentoxide to 7,15-dihydrodinaphtho[1,2-*a*:1′,2′-*g*]-s-indacene (X),



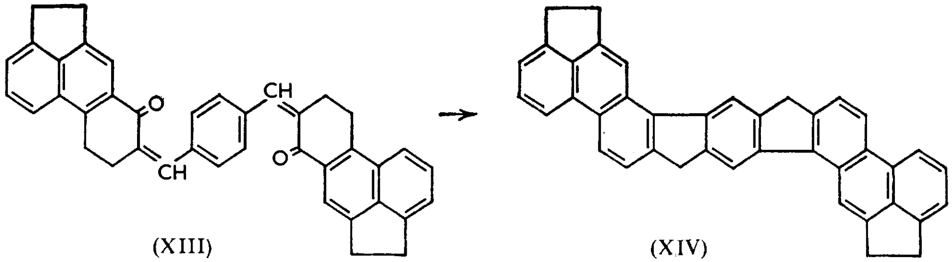
(IX) (X)

in low yield. From terephthalaldehyde and 1,2,3,4-tetrahydro-1-oxophenanthrene, the compound (XI) was similarly prepared and cyclised to the diphenanthro-*s*-indacene (XII);



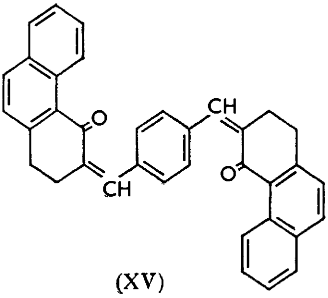
(XI) (XII)

from 2,8,9,10-tetrahydro-7-oxoacephenanthrene, compound (XIV) was obtained *via* the "chalcone" (XIII).

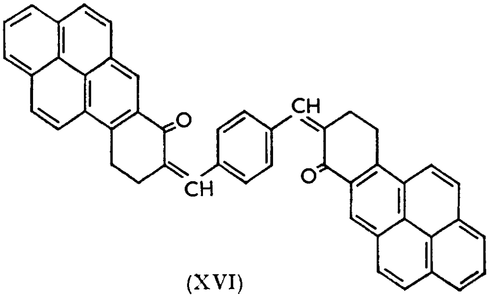


(XIII) (XIV)

Terephthalaldehyde underwent reaction of both its aldehyde groups with other condensed cyclanones, such as 1,2,3,4-tetrahydro-4-oxophenanthrene and 7,8,9,10-tetrahydro-7-oxobenzo[*a*]pyrene to give compounds (XV) and (XVI) respectively; with heterocyclic

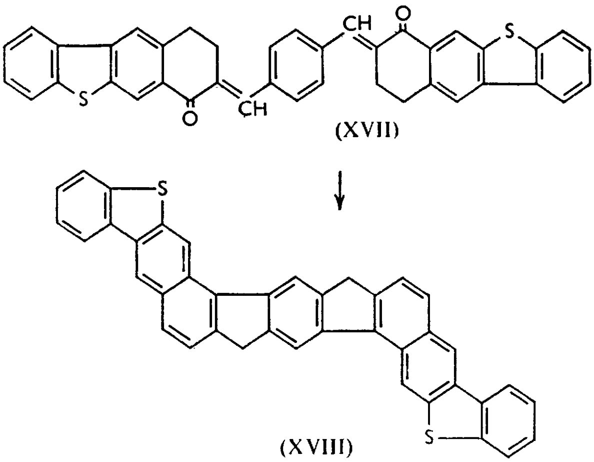


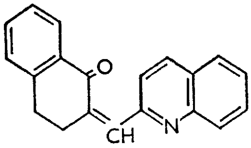
(XV)



(XVI)

ketones it also underwent double condensation, resulting in compounds such as (XVII), whose cyclisation afforded compound (XVIII).





(XIX)

With a view to extending the Rapson–Shuttleworth reaction to the synthesis of azabenzofluorene derivatives, quinoline-2-aldehyde was condensed with α-tetralone to give ketone (XIX); the last compound, however, resisted cyclodehydration and was recovered unchanged after treatment with phosphorus pentoxide. Similar failure was encountered with the condensation products of quinoline-2-aldehyde with 7-methyl-1-tetralone, 1,2,3,4-tetrahydro-1- and -4-oxophenanthrene, 7,8,9,10-tetrahydro-7-oxoacephenanthrene, 7,8,9,10-tetrahydro-7-oxobenzo[*a*]pyrene, and 7,8,9,10-tetrahydro-7-oxobenzo[*b*]naphtho[2,3-*d*]-thiophen. The inability of ketones of the type of (XIX) to undergo cyclodehydration might be considered a consequence of Marckwald's rule, which, with reference to the quinoline nucleus, excludes easy cyclisation across the 2,3-bond.[3]

EXPERIMENTAL

2-4'-*Isopropylbenzylidene*-1-*tetralone*.—4-Isopropylbenzaldehyde (5 g.; freshly redistilled) and 1-tetralone (5 g.) were shaken for 5 min. with 4% ethanolic potassium hydroxide (50 c.c.), and the mixture was left in the refrigerator for 3 days. After addition of water, the product was taken up in benzene, the benzene solution washed first with aqueous acetic acid, then with water, dried (Na_2SO_4), and evaporated, and the residue fractionated *in vacuo*. The condensation *product* (6 g.) had b. p. 267°/17 mm., n_D^{28} 1·6515 (Found: C, 86·8; H, 7·3. $C_{20}H_{20}O$ requires C, 86·9; H, 7·3%).

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[3] For discussion of this rule, see Badger, " The Structures and Reactions of the Aromatic Compounds," Cambridge University Press, 1954, p. 116.

10-*Isopropyl*-7H-*benzo*[c]*fluorene* (I).—A solution of the foregoing ketone (5·5 g.) in anhydrous xylene (60 c.c.) was refluxed for 30 hr. with phosphorus pentoxide (6 g.); the supernatant liquid was decanted, washed with aqueous sodium hydroxide, then with water, and dried (Na_2SO_4), the solvent was removed, and the residue fractionated *in vacuo*. The portion of b. p. 185—190°/0·3 mm. was purified *via* its picrate, and recrystallised from ethanol as needles (2 g.), m. p. 98—99°, highly soluble in benzene (Found: C, 93·1; H, 7·0. $C_{20}H_{18}$ requires C, 93·0; H, 7·0%).

2-4′-*Isopropylbenzylidene*-7-*methyl*-1-*tetralone*.—Prepared as above from 4-isopropylbenzaldehyde (5 g.), 7-methyl-1-tetralone (5·8 g.), and 4% ethanolic potassium hydroxide (25 c.c.), this *ketone*, b. p. 277°/16 mm., formed prisms (6 g.), m. p. 96°, from aqueous ethanol (Found: C, 86·9; H, 7·6. $C_{21}H_{22}O$ requires C, 86·9; H, 7·6%); its solutions in sulphuric acid were orange-yellow.

2-*Methyl*-10-*isopropyl*-7H-*benzo*[c]*fluorene* (II).—Cyclodehydration of the foregoing compound (5·5 g.) with phosphorus pentoxide (6·5 g.) gave this *hydrocarbon*, needles (0·8 g.), m. p. 116° (from ethanol) (Found: C, 92·6; H, 7·3. $C_{21}H_{20}$ requires C, 92·6; H, 7·4%).

7,8,9,10-*Tetrahydro*-8-4′-*isopropylbenzylidene*-7-*oxoacephenanthrene* (III).—Prepared from the aldehyde (2 g.) and 7,8,9,10-tetrahydro-7-oxoacephenanthrene (3 g.), this *ketone* formed leaflets (4 g.), m. p. 141°, from ethanol (Found: C, 88·6; H, 6·9. $C_{26}H_{24}O$ requires C, 88·6; H, 6·9%).

1,2-*Dihydro*-11-*isopropyl*-8H-*acenaphtho*[4,5-c]*fluorene* (IV).—This *hydrocarbon*, obtained *via* its brown-red picrate, formed colourless needles, m. p. 204°, from ethanol (Found: C, 93·4; H, 6·6. $C_{26}H_{22}$ requires C, 93·4; H, 6·6%).

8-4′-*Isopropylbenzylidene*-7,8,9,10-*tetrahydro*-7-*oxobenzo*[b]*naphtho*[2,3-d]*furan*. Prepared from cuminaldehyde (2 g.) and ketone (V) (3·6 g.), this *ketone* formed from ethanol pale yellow prisms (4 g.), m. p. 179°, whose solutions in sulphuric acid were cherry-red (Found: C, 85·1; H, 5·9. $C_{26}H_{22}O_2$ requires C, 85·2; H, 6·0%).

2-*Isopropylfluoreno*[3′,4′-4,5]*dibenzofuran* (VII).—Prepared by cyclisation of the foregoing ketone (3·2 g.), this *compound* was purified *via* its brown picrate, and formed yellow needles (0·3 g.), m. p. 214°, from ethanol–benzene (Found: C, 89·6; H, 5·8. $C_{26}H_{20}O$ requires C, 89·6; H, 5·7%).

8-4′-*Isopropylbenzylidene*-7,8,9,10-*tetrahydro*-7-*oxobenzo*[b]*naphtho*[2,3-d]*thiophen*.—Prepared from ketone (VI) (4 g.) and the aldehyde (2·5 g.), this *ketone* formed from ethanol pale yellow prisms (5 g.), m. p. 165—166°, whose solutions in sulphuric acid were deep pink (Found: C, 81·4; H, 5·8. $C_{26}H_{22}OS$ requires C, 81·7; H, 5·8%).

2-*Isopropylfluoreno*[3′,4′-4,5]*dibenzothiophen* (VIII).—This *compound*, b. p. 260°/0·5 mm., formed cream-coloured needles, m. p. 193°, from cyclohexane (Found: C, 85·8; H, 5·6. $C_{26}H_{20}S$ requires C, 85·7; H, 5·5%).

p-*Phenylene*(*di*-2-*methylene*-1-*tetralone*) (IX).—Prepared in the usual way from terephthalaldehyde (3 g.), 1-tetralone (7·5 g.), and 4% ethanolic potassium hydroxide (50 c.c.), this *product* formed from ethanol–benzene yellow prisms (8·5 g.), m. p. 282°, whose solutions in sulphuric acid were cherry-red (Found: C, 86·0; H, 5·6. $C_{28}H_{22}O_2$ requires C, 86·1; H, 5·7%).

7,15-*Dihydrodinaphtho*[1,2-a:1′,2′-g]-*s*-*indacene* (X).—Prepared by cyclodehydration of the foregoing compound (7·5 g.) with phosphorus pentoxide (11 g.) in xylene (75 c.c.), this *hydrocarbon* formed pale yellow needles (0·1 g.), m. p. 303°, from ethanol–benzene (Found: C, 94·9; H, 5·1. $C_{28}H_{18}$ requires C, 94·9; H, 5·1%).

7,17-*Dihydrodiphenanthro*[1,2-a:1′,2′-g]-*s*-*indacene* (XII).—The *compound* (XI), prepared from 1,2,3,4-tetrahydro-1-oxophenanthrene (3·5 g.) and terephthalaldehyde (1·3 g.), formed from ethanol–benzene yellow prisms (3·8 g.), m. p. 230°, whose solutions in sulphuric acid were violet (Found: C, 88·3; H, 5·5. $C_{36}H_{26}O_2$ requires C, 88·1; H, 5·3%). Cyclodehydration of it yielded the *hydrocarbon* (XII), crystallising as colourless needles, m. p. 267°, from ethanol–benzene (Found: C, 95·3; H, 4·9. $C_{36}H_{22}$ requires C, 95·1; H, 4·9%). The *compound* (XV), similarly prepared from 1,2,3,4-tetrahydro-4-oxophenanthrene and terephthalaldehyde, crystallised as yellow prisms, m. p. 155—156°, from ethanol–benzene (Found: C, 88·1; H, 5·4. $C_{36}H_{26}O_2$ requires C, 88·1; H, 5·3%). The *analogue* (XVI), prepared from 7,8,9,10-tetrahydro-7-oxobenzo[*a*]pyrene (1·5 g.) and terephthalaldehyde (0·5 g.), formed yellow leaflets (1·2 g.), m. p. 253° (from ethanol–benzene), which gave brown-red solutions in sulphuric acid (Found: C, 90·2; H, 4·9. $C_{48}H_{30}O_2$ requires C, 90·3; H, 4·7%).

8,18-*Dihydrodiacephenanthro*[4,5-a:4′,5′-g]-*s*-*indacene* (XIV).—The *compound* (XIII), prepared from terephthalaldehyde (1·8 g.) and 7,8,9,10-tetrahydro-7-oxoacephenanthrene (6 g.), formed from ethanol–benzene deep yellow prisms (6 g.), m. p. 231°, giving violet-brown solutions in sulphuric acid (Found: C, 88·4; H, 5·6. $C_{40}H_{30}O_2$ requires C, 88·5; H, 5·6%). The *hydrocarbon* (XIV) obtained on its cyclodehydration formed pale yellow prisms, m. p. 318°, from ethanol–benzene (Found: C, 94·7; H, 5·2. $C_{40}H_{26}$ requires C, 94·8; H, 5·2%).

8,18-*Dihydrodibenzo*[4‴,5‴:4⁗,5⁗]*dithieno*[2‴,3‴-6,7:2⁗,3⁗-6′,7′]*dinaphtho*[1,2-*a*:1′,2′-*g*]-*s-indacene* (XVIII).—The *compound* (XVII), prepared from ketone (VI) (5·3 g.) and terephthalaldehyde (1·5 g.), formed from ethanol–benzene greenish-yellow prisms (5 g.), m. p. 228°, whose solutions in sulphuric acid were violet (Found: C, 80·3; H, 4·4. $C_{40}H_{26}O_2S_2$ requires C, 79·7; H, 4·3%). Cyclodehydration furnished *compound* (XVIII), crystallising as orange prisms, m. p. >320°, from benzene (Found: C, 84·6; H, 4·1. $C_{40}H_{22}S_2$ requires C, 84·8; H, 3·9%).

2-(1-*Oxo*-2-*tetralylidenemethyl*)*quinoline* (XIX).—A solution of 1-tetralone (8 g.) and quinoline-2-aldehyde (10 g.) in 4% ethanolic potassium hydroxide (100 c.c.) was shaken for 10 min., then left for 12 hr. at room temperature. The precipitate was washed with water and recrystallised from ethanol, giving pale yellow needles (10·5 g.), m. p. 125°, whose solutions in sulphuric acid were orange-yellow (Found: C, 84·2; H, 5·4. $C_{20}H_{15}NO$ requires C, 84·2; H, 5·3%). The derived *picrate* formed yellow prisms, m. p. 175°, from ethanol (Found: N, 10·9. $C_{26}H_{18}N_4O_8$ requires N, 10·9%). Several attempts to cyclise this product (12 g.) with phosphorus pentoxide (12 g.) in xylene (75 c.c.) gave only unchanged starting material: use of sodamide was equally unsuccessful.

2-(7-*Methyl*-1-*oxo*-2-*tetralylidenemethyl*)*quinoline*.—Prepared from 7-methyl-1-tetralone (10·5 g.) and quinoline-2-aldehyde (10 g.), this *compound* formed yellow needles (13 g.), m. p. 129°, from ethanol (Found: C, 84·3; H, 5·9. $C_{21}H_{17}NO$ requires C, 84·3; H, 5·7%). The *picrate* crystallised as orange-yellow prisms (from ethanol), m. p. 191° (Found: N, 10·3. $C_{27}H_{20}N_4O_8$ requires N, 10·6%).

2-(1,2,3,4-*Tetrahydro*-1-*oxophenanthrylidenemethyl*)*quinoline*.—Prepared from 1,2,3,4-tetrahydro-1-oxophenanthrene (1 g.) and quinoline-2-aldehyde (0·8 g.), this *ketone* formed yellow needles (0·6 g.), m. p. 176°, from ethanol (Found: C, 85·9; H, 5·4. $C_{24}H_{17}NO$ requires C, 85·9; H, 5·1%). The 4-*oxo-analogue*, obtained similarly, formed yellow needles, m. p. 166°, from ethanol (Found: C, 85·9; H, 5·2%).

2-(2-*Quinolylmethylene*)-1,2,3,4-*tetrahydro*-1-*oxoacephenanthrene*.—From 1,2,3,4-tetrahydro-1-oxoacephenanthrene (2 g.) and quinoline-2-aldehyde (1·5 g.), this *ketone* formed yellow needles (2 g.), m. p. 207°, from ethanol–benzene (Found: C, 86·3; H, 5·0. $C_{26}H_{19}NO$ require C, 86·4; H, 5·3%). The *picrate* formed orange-red needles, m. p. 188°, from ethanol–benzene (Found: N, 9·5. $C_{29}H_{22}N_4O_8$ requires N, 9·5%).

2-(7,8,9,10-*Tetrahydro*-7-*oxobenzo*[a]*pyrenylidenemethyl*)*quinoline*.—Prepared from the oxobenzopyrene (3 g.) and quinoline-2-aldehyde (2 g.), this *compound* formed deep yellow needles (3 g.), m. p. 221°, from ethanol–benzene (Found: C, 88·1; H, 4·8. $C_{30}H_{19}NO$ requires C, 88·0; H, 4·6%), and gave a *picrate*, orange-red prisms (from ethanol–benzene), m. p. 185° (Found: N, 8·8. $C_{36}H_{22}N_4O_8$ requires N, 8·8%).

8-(2-*Quinolylmethylene*)-7,8,9,10-*tetrahydro*-7-*oxo*[b]*naphtho*[2,3-d]*thiophen*.—Prepared from ketone (VI) (2 g.) and quinoline-2-aldehyde (1·3 g.), this *compound* formed yellow needles (2 g.), m. p. 265°, from ethanol–benzene (Found: C, 79·8; H, 4·4. $C_{26}H_{17}NOS$ requires C, 79·8; H, 4·3%).

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