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POLYNUCLEAR AROMATIC HYDROCARBONS—XI

CHRYSENE DERIVATIVES

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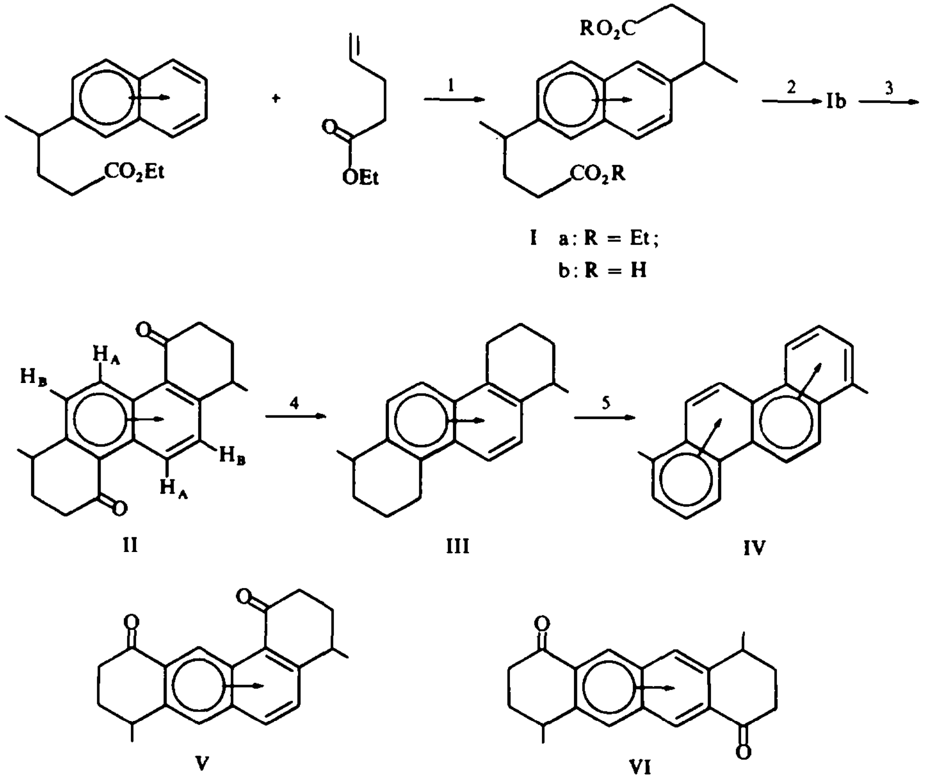
Abstract—A convenient synthesis of 3,9-dimethylchrysene is described.

NAPHTHALENE undergoes aluminium chloride-catalysed alkylation with ethyl allylacetate at the 2-position.[1] Since acid-catalysed alkylation of 2-alkylnaphthalenes takes place preferentially at the 6-position[2] of the naphthalene moiety it was thought feasible that double condensation of naphthalene with ethyl allylacetate would be a convenient route to chrysene derivatives according to the following reaction sequences:



I a: R = Et;
b: R = H

II

III

IV

V

VI

1, $AlCl_3$–CS_2; 2, KOH–EtOH; 3, PPA; 4, Zn(Hg)–HCl; 5, Pd–C.

Ethyl γ-(2-naphthyl)valerate[1] was treated with ethyl allylacetate in presence of anhydrous $AlCl_3$ according to the procedure prescribed.[1] when the diester Ia was obtained in 32% yield, the homogeneity of the product being confirmed through TLC. The diester was hydrolysed with alcoholic KOH and the resulting diacid Ib cyclized with PPA to effect a double cyclization giving the diketone II in 66% yield as the exclusive product. A similar double cyclization of γ,γ′-(2,6-naphthylene)dibutyric acid by treatment of its acid chloride with $SnCl_4$ to give exclusively the chrysene derivative has recently been reported.[3] Of the three possible structures for our diketone, namely, II, V and VI, the structure II is confirmed on the basis of its 40 Mc NMR spectrum in $CHCl_3$ which shows a doublet at 9·4 ppm ($J = 9$ c/s; orthocoupling) due to the H_A protons, deshielded by the two CO groups at the *peri* and *para* positions to the extent of 78 c/s;[*] a doublet at 7·45 ppm ($J = 9$ c/s; orthocoupling) due to the H_B protons characteristic of AB system; and a doublet at 1·43 ppm ($J = 6·8$ c/s; vicinal coupling) due to the 6 Me-protons split into a doublet by the two vicinal protons.

The diketone II was reduced by the Martin's modification of Clemmensen reduction to furnish the corresponding octahydrochrysene derivative III in 88% yield which underwent smooth dehydrogenation with 30% Pd–C. The dehydrogenation product did not give a stable picrate which, however, could be prepared below 0° and the crude picrate on passing through a column of basic alumina furnished pure 3,9-dimethylchrysene (IV).

EXPERIMENTAL[†]

Diethyl γ,γ-(2,6-naphthylene)divalerate (Ia). Ethyl γγ′-(2-naphthyl)valerate (21 g) reacted with ethyl allylacetate (10·5 g) in CS_2 (80 ml) in presence of anhyd $AlCl_3$ (21 g) according to the conditions prescribed.[1] After removal of the solvent the residual viscous liquid was distilled and chromatographed over silica gel eluted with pet. ether (60–80°); b.p. 240–242° 2 mm; yield: 10 g (32%). (Found: C, 75·03; H, 8·403. Calc. for $C_{24}H_{32}O_4$: C, 75·00; H, 8·33%).

γ,γ′-(2,6-*Naphthylene)divaleric acid* (Ib). Hydrolysis of Ia (9·0 g) with 20% alcoholic KOH (from 10 g KOH) was effected by refluxing for 13 hr to obtain Ib, b.p. 280°/2 mm; yield 7 g (91%). (Found: C, 73·64; H, 6·8. Calc. for $C_{20}H_{24}O_4$: C, 73·174; H, 7·31%).

6,12-*Dioxo*-3,9-*dimethyl*-3,4,5,6,9,10,11,12-*octahydrochrysene* (II). The acid Ib (6 g) reacted with PPA (from P_2O_5 (36 g) and H_3PO_4 (27 ml)) at 145°.[4] The product was extracted with ether, washed successively with 5% NaOHaq 5% AcOHaq, water, 10% $NaHCO_3$aq and water, and dried over $MgSO_4$. After removal of the solvent the residual material solidified. It was recrystallized from pet ether (60–80°) benzene to afford 3·5 g (66%) of II, m.p. 176° (single spot on TLC; EtOAc–benzene (1:9)). (Found: C, 81·70; H, 7·3. Calc. for $C_{20}H_{20}O_2$: C, 82·19; H, 6·85%); UV spectrum (EtOH): 243·5 (log ε 4·69) (cyclic αβ-unsaturated ketone),[5] 304 (log ε 4·01), 314·5 (log ε 4·12) and 333 (log ε 4·03) mμ; IR (Nujol): 2910 (s), 1975 (w), 1810 (w), 1660 (s) (αβ-unsaturated ketone),[6] 1580 (s), 1360 (m), 1195 (s), 1110 (s) cm^{-1}.

3,9-*Dimethyl*-3,4,5,6,9,10,11,12-*octahydrochrysene* (III). The diketone II (1·5 g) when reduced with ZnHg (15 g), conc HCl (20 ml), AcOH (10 ml) and toluene (10 ml) by refluxing for 30 hr yielded 1·2 g (88%) of a colourless liquid distilling at 225–227°/2 mm. (Found: C, 90·40; H, 8·53. Calc. for $C_{20}H_{24}$: C, 90·90; H, 9·10%).

3,9-*Dimethylchrysene* (IV). Compound III (1·0 g) was treated with 30% Pd–C (0·1 g) for 3 hr at 300–340°, and converted into the picrate at 0–5° and the crude product decomposed by passing through a column of basic alumina and the regenerated hydrocarbon was crystallized from EtOH to furnish 0·6 g (62%) of

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[*] Calculated value on the basis of the data reported by Martin *et al.* (*Tetrahedron* **20**, 1005 (1964) for the deshielding effect of the CO on the *peri* position and that of another CO on the same proton in *para* position comes to 72 c/s.

[†] B.ps and m.ps are uncorrected.

TLC pure (pet ether b.p. 60–80°) IV m.p. 129°. The hydrocarbon did not give a stable picrate. (Found: C, 93·38; H, 6·7. Calc. for $C_{20}H_{16}$: C, 93·75; H, 6·25%); UV spectrum (EtOH): 240 (log ε 4·4), 264 (log ε 4·7), 275 (log ε 4·87), 291 (log ε 4·36), 303 (log ε 4·20), 316 (log ε 4·02), 332 (log ε 3·94), 369 (log ε 3·38), 389 (log ε 3·54) and 410 (log ε 3·71) mμ; IR (Nujol): 2910 (s) (CH_3), (1935–1700 (aromatic bands)), 1610 (s), 1595 (s), 1420 (s), 1260 (s), 835 (s) and 765 (s) cm^{-1}.

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