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Synthesis of substituted 3′, 4′ -dihyrospiro [indane-1, 2′(1′*H*) naphthalene]-1′-ols and their catalytic dehydrogenation

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Catalytic dehydrogenation of 5′, 7′-dimethyl-3′, 4′-dihydrospiro[indane-1, 2′(1′*H*) naphthalene]-1′-ol **5a**, 7′-ethyl-3′,4′-dihydrospiro[indane-1, 2′-(1′H) naphthalene]-1′-ol **5b**, 6-methyl-3′, 4′-dihydrospiro[indane-1, 2′(1′*H*) naphthalene]-1′-ol **5c** and 6, 7′-dimethyl-3′, 4′-dihydrospiro[indane-1, 2′(1′*H*) naphthalene]-1′-ol **5d** affords 1, 3-dimethylchrysene **6a**, a mixture of 3-ethyl chrysene **6b** and chrysene, 3-methylchrysene **6c** and 3, 9-dimethylchrysene **6d**, respectively. Condensation of anhydride of **1a** of 1-carboxyindane-1-acetic acid with *m*-xylene and ethylbenzene give ketoacids **2a** and **2b** while **2c** and **2d** are obtained by condensation of the anhydride **1b** of 1-carboxy-6-methylindane-1-acetic acid with benzene and toluene respectively. Catalytic reduction in acetic acid solution of **2a, 2c, 2d**, and in ethanolic solution of **2b**, give **3a**, **3c**, **3d** and **3b**. In ethanolic solution, **2c** and **2d** give esters $\mathbf{3c_E}$ and $\mathbf{3d_E}$. Intramolecular acylation of **3a**, **3b**, **3c** and $\mathbf{3c_E}$ and **3d** and $\mathbf{3d_E}$ give **4a**, **4b**, **4c** and **4d** which after LAH reduction followed by dehydrogenation gave chrysenes **6a**, **6b**, **6c** and **6d**. Structures of all compounds corroborate their spectral data.

Ring transformation with formation of fully aromatic compound is encountered in the dehydrogenation of spirans with selenium, sulphur or platinum and palladium on charcoal[1-6]. It was previously observed that during catalytic dehydrogenation of spirocompounds the nature and the position of the substituent as also the nature of the catalyst control the course of rearrangement. Clemo and Ormston[1] obtained naphthalene in the dehydrogenation of spiro[cyclopentane-1, 2′-cyclohexane] system. Sengupta and Chatterjee[4] observed that the methyl group at 2-position of the system was retained in fully aromatic hydrocarbon phenanthrene while with ethyl group in 2-position it afforded pyrene. Chatterjee[5] also obtained methylpyrene from the corresponding 2-propyl spiran.

The present investigation aims at studying the effect and fate of alkyl group in one or more positions of 3′, 4′-dihydrospiro[indane-1, 2′(1′*H*) naphthalene]-1′-ol system on the mode of molecular rearrangement during their catalytic dehydrogenation. Thus we have synthesised 5′, 7′-dimethyl (**5a**), 7′-ethyl (**5b**), 6-methyl (**5c**) and 6, 7′-dimethyl (**5d**) derivatives of 3′, 4′-dihydrospiro[indane-1, 2′(1′*H*) naphthalene]-1′-ol.

Spirocarbinols **5a** and **5b** were synthesised by the following steps: Anhydride **1a** of 1-carboxyindane-1-acetic acid was condensed with *m*-xylene and with ethylbenzene under Friedel-Crafts condition to give α,α-(1′-indane)-β-(2, 4-dimethyl benzoyl) propanoic acid (**2a**) and αα-(1′-indane)-β-(*p*-ethylbenzoyl)propanoic acid (**2b**) while condensation of the anhydride **1b** of 1-carboxy-6-methylindane-1-acetic acid with benzene and with toluene gave αα-(6-methylindane)-β-benzoyl propanoic acid **2c** and αα-(6-methylindane)-β-(*p*-toluyl) propanoic acid **2d**. The keto-acids **2a**, **2c** and **2d** were successfully catalytically reduced in acetic acid containing a few drops of perchloric acid in the presence of Pd-C at 50-60° and 50 psi of hydrogen to 2′, 4′-dimethyl (**3a**), 5-methyl (**3c**), 6, 4′-dimethyl (**3d**) substituted α,α-(1-indane)-γ-phenylbutyric acids. Keto-acid **2b** in absolute ethanol under similar conditions was reduced to 4′-ethyl-(**3b**) while **2c**

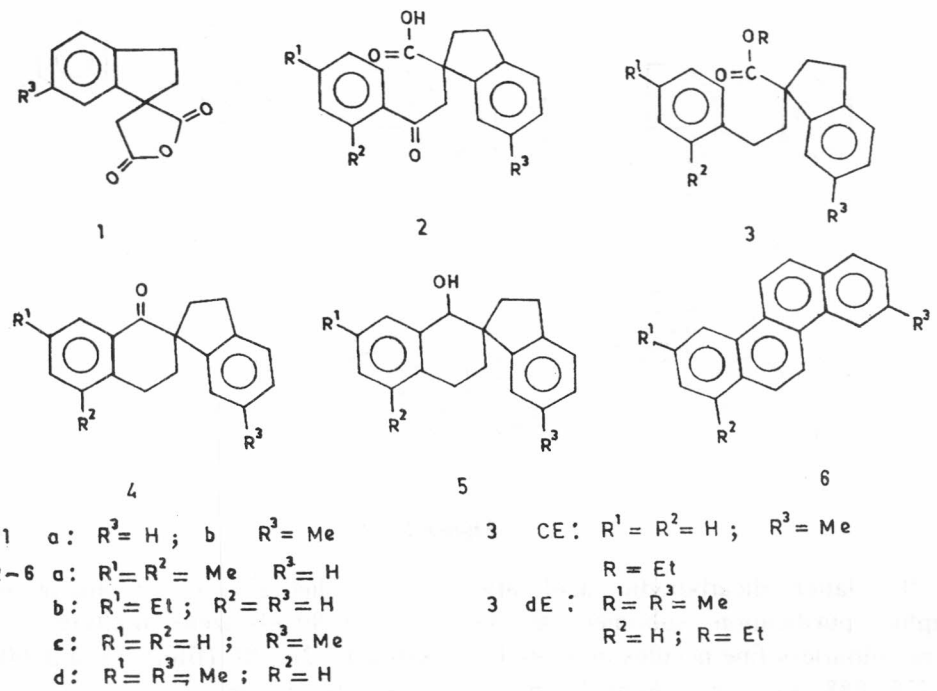

Figure 1

and **2d** in dry ethanol formed the corresponding ethyl esters $\mathbf{3c_E}$ and $\mathbf{3d_E}$ of α,α-(1-indane)-γ-phenylbutyric acids. The acid chlorides of phenyl butyric acids **3a, 3b, 3c** and **3d** under Friedel-Crafts intramolecular acylation gave the corresponding spiroketones 5′, 7′-dimethyl-(**4a**), 7′-ethyl-(**4b**), 6′-methyl-(**4c**) and 6, 7′-dimethyl-(**4d**) substituted 3′, 4′-dihydro-1′-ketospiro[indane-1, 2′-(1′*H*) naphthalene] derivatives. Intramolecular acylation with polyphosphoric acid of acid **3a**, ethylesters $\mathbf{3c_E}$ and $\mathbf{3d_E}$ afforded the spiroketones **4a, 4c** and **4d** in good yield. Spiroketones **4a, 4b, 4c** and **4d** were reduced with LAH to the title compounds **5a, 5b, 5c** and **5d** (Figure 1).

In the present investigation it was observed that dehydrogenation of **5a, 5b, 5c** and **5d** when separately heated with Pd-C (10%) at 380-390° in sealed tubes afforded 13-dimethyl (**6a**), 3-ethyl-(**6b**), with a trace of chrysene, 3-methyl-(**6c**) and 3, 9-dimethylchrysene (**6d**) respectively. In each of these cases, it was observed that aromatisation took place without any loss of carbon atom, but in the dehydrogenation of **5b** small amount of chrysene was also formed with the loss of two carbon atoms. The rearrangement can be rationalised as follows. At first dehydrogenation of the carbinols takes place to form (**A**) which then undergoes ring cleavage of the spirocyclopentane ring between the spirocarbon and the carbon atom away from the fused benzene ring to give a diradical **B**. The diradical passes on to the diradical **C** which then cyclises in an angular manner to form the partially reduced chrysene **D**. This is then dehydrogenated to afford aromatic hydrocarbon **E** (Figure 2). In the dehydrogenation of **5b**, a portion of the reduced chrysene nucleus **D** also knocked off ethyl group to form chrysene with the loss of two carbon atoms.

Experimental Section

Mps were obtained in open capillary tubes and are uncorrected. PMR and IR spectra were recorded at CDRI, Lucknow and IICB, Calcutta.

1-Carboxy-indane-1-acetic acid and its 6-methyl derivative required for the present investigation were prepared by condensation of ethyl cyanoacetate with the corresponding ketones according to the method of Lapworth and Mcrae[6], Harding and Haworth[7], as improved by Cope[8] followed by cyanide addition to ethylindenylidene cyanoacetates and subsequent hydrolysis with concentrated hydrochloric acid. 1-Carboxy-indane-1-acetic acid crystallised from benzene-petroleum ether, m.p. 175-76° and its 6-methyl derivative (colourless crystals) melted at 193-95°. The methyl

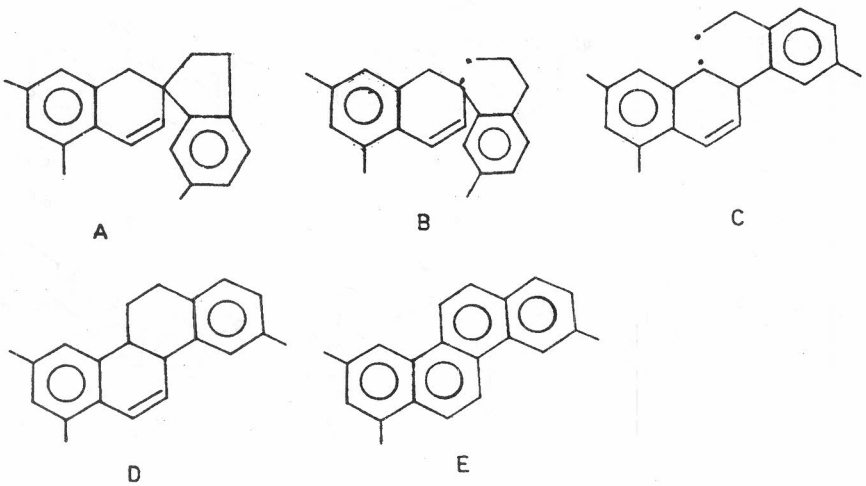

Figure 2

ester of the latter dicarboxylic acid after chromatographic purification sublimed at 89-90°/0.3 mm as colourless fine needles m.p. 90-91°; IR (KBr): 1725, 888, 825 cm^{-1} (Anal. Found: C, 68.48; H, 7.11. Calc. for $C_{15}H_{18}O_4$ C, 68.68; H, 6.92. The anhydrides **1a** and **1b** were obtained by heating under reflux the corresponding acids with acetic anhydride, and **1a** collected at 170-75°/1.5 mm which soon solidified, m.p. 63-64° and **1b** separated as colourless crystals m.p. 125-27°; b.p. 165°/0.6 mm; IR (KBr) : 1875, 1790, 930, 885, 818 cm^{-1}. Anhydride **1b** on refluxing with aniline in benzene gave anilic acid which crystallised from benzene, m.p. 195°; IR (KBr): 3300 (N-H), 3125 (OH of acid), 1700, 1650 ($-CONH_2$), 900, 820 cm^{-1}. Anal. Found: C, 73.76; H, 6.02; N, 4.64. Calc. for $C_{19}H_{19}NO_3$: C, 73.76; H, 6.19; N, 4.53.

α, α–(1–**Indane)-β-(2,4-dimethylbenzoyl)propanoic acid 2a**. Anhydrous aluminium chloride (12g) was gradually added to a well stirred solution of the anhydride **1a** (8g) of 1-carboxyindane-1-acetic acid and dry *m*-xylene (8 mL) in dry *sym*-tetrachloroethane (40 mL) cooled in ice. The reaction mixture was allowed to stand overnight at room temperature and then warmed at 50-60°C for 0.5 hr till the evolution of hydrogen chloride ceased. Decomposition with ice and HCl and usual work-up gave a gum. This was collected and dissolved in hot dilute sodium bicarbonate solution (charcoal) and filtered. The ketoacid separated as a heavy viscous mass, which was extracted with benzene and the benzene extract was washed with water, dried (Na_2SO_4) and the solvent removed. The residual gum was chromatographed [silica gel, pet (60-80°)-benzene mixture 1:1] to get pure ketoacid **2a**; IR (film) 3330-2700, 1710 (C=O), 830, 760, 730 cm^{-1}.

Similarly, α,α–(1–indane)–β–(*p*-ethylbenzoyl)-propanoic acid **2b** (20 g) was obtained by condensation of **1a** (30 g) with ethylbenzene (25 mL) in nitrobenzene (50 mL) and *sym*-tetrachloroethane (25 mL) and collected at 200-5°/0.5 mm as a thick colourless liquid.

Ketoacid **2c** (15 g) was obtained similarly from condensation of anhydride **1b** (22 g) in benzene (120 mL) and collected at 170-80°/1.5 mm as yellow viscous oil which readily solidified and was crystallised from benzene as colourless needles, m.p. 116-8°; IR (KBr): 3500-2900, 1710 (C=O), 885, 820 (1, 2, 4-trisubstituted benzene), 757, 710 cm^{-1} (monosubstituted benzene); UV (EtOH): 225 (log ε 3.14), 272 (3.32), 304 (1.74) nm. Condensation of **1b** (20 g) with toluene (15 mL) in *sym*-tetrachloroethane (60 mL) in presence of aluminium chloride gave the ketoacid **2d** (12 g) collected at 150-55°/0.5 mm; and crystallised from benzene as a white power, m.p. 168-69°; IR (KBr): 3300-25000, 1710 (C=O), 845, 835, 810 cm^{-1}. Anal. Found: C, 77.72; H, 6.29. Calc. for $C_{20}H_{20}O_3$, requires C, 77.90; H, 6.54%.

Crimson red pyrylium salts of ketoacids **2a**, **2b**, **2c** and **2d** separated when solution containing ketoacids (0.1 g) and salicylaldehyde (0.1 g) in absolute ethanol were saturated with dry hydrogen chloride and kept in a refrigerator for three days.

They were readily soluble in alkali and did not melt upto 250°.

α,α-(1-Indane)-γ-(2,4-dimethylphenyl)butyric acid 3a. A solution of ketoacid **2a** (9g) in glacial acetic acid (60 mL) containing a few drops of perchloric acid and palladised charcoal (1.2 g; 10%) was stirred at 60-65° in an atmosphere of hydrogen at 50 psi when the required amount of hydrogen was absorbed. The usual work-up gave the reduced acid **3a** (8g) which was collected by short path distillation at 180-85°/0.5 mm (metal bath temperature) as a viscous mass; IR (film): 3300-2700, 1710, 850, 820 and 745 cm^{-1}.

In a similar way, ketoacid **2b** (16g) in ethanolic solution gave reduced acid **3b** (11g) and was collected at 182-85°/0.5 mm as a thick colourless liquid. Anal. Found: C, 81.18; H, 7.31. Calc. for $C_{20}H_{22}O_2$: C, 81.63; H, 7.48%. Compound **2c** (10 g) in glacial acetic acid solution was reduced under similar condition to butyric acid **3c** (solid) which was crystallised from pet. ether (60-80°) as white needles, m.p. 110-12°; yield 7g. IR (KBr): 3200-2700, 1700, 880, 818, 742, 710 cm^{-1}. Anal. Found: C, 80.97; H, 6.90. Calc. for $C_{19}H_{20}O_2$. C, 81.39; H, 7.19%. Compound **2c** in dry ethanol (100 mL) under similar conditions gave the corresponding ethyl butyrate $\mathbf{3c_E}$ (12g), a colourless fluid oil, b.p. 130°/0.3 mm IR (film): 1745, 1250, 1175, 880, 820, 755, 705 cm^{-1}; PMR ($CDCl_3$); δ 1.25 (3H, t, $-O-CH_2CH_3$), 1.3-1.9 (4H, m, aliphatic, alicyclic), 2.31 (3H, s, $ArCH_3$), 2.5-2.95 (4H, m, benzylic), 4.15 (2H, q, *J*=7 Hz, $-OCH_2CH_3$), 6.95-7.3 (8H, m, aromatic). Compound **2d** (10 g) in acetic acid under similar conditions was reduced to butyric acid **3d** (7g), a solid which was crystallised from benzene-petroleum ether (40-60°) as colourless crystals, m.p. 151-53°; IR (KBr) : 3250-2550, 1700, 880, 815 cm^{-1}. Anal. Found : C, 81.41; H, 7.32. Calc. for $C_{20}H_{22}O_2$ C, 81.60; H, 7.53%. Compound **2d** (15g) in dry ethanol was reduced under similar conditions to ethyl butyrate $\mathbf{3d_E}$ (9g) as a colourless oil with a blue fluorescence, b.p. 130°/0.3 mm; IR (film): 1740, 1200, 1175, 820 cm^{-1}; PMR ($CDCl_3$): δ6.70-7.20 (7H, m, ArH), 4.15 (2H, q, *J*=7 Hz, $-O-CH_2-CH_3$), 2.45-3.00 (4H, m, benzylic), 2.29 (6H, s, 2 $Ar.CH_3$), 1.05-1.70 (7H, m, aliphatic and alicyclic).

Formation of spiroketone. The acid **3a** (8g) was converted into acid chloride by thionyl chloride (10 mL) following a standard procedure. To the cold solution of the acid chloride in pet. ether (60-80°, 50 mL) anhyd. $AlCl_3$ (8g) was added in portion with constant stirring. The reaction mixture was kept at 60-65° for 2 hr, and then refluxed on a steam-bath for 6 hr. The mixture was decomposed with ice and HCl and extracted with ether. The ether extract was successively washed with water, aq. NH_3 and finally with water till neutral, dried and the solvent removed. The residual oil was purified by chromatography (Al_2O_3; petroleum ether 60-80°) and distilled to get the spiroketone **4a** (3g), b.p. 180-90°/1 mm.

The acid **3a** (8g) was stirred with polyphosphoric acid (P_2O_5, 50g; H_3PO_4, 30 mL) heated on a steam-bath for 2 hr. After usual work-up, it was extracted with ether. The ether extract was sequentially washed with water, alkali and water, dried and the solvent removed. The residual oil was distilled to get the spiroketone **4a** (4.8g) at 180-90°/l mm; IR: 1675 (C=O), 870 (1, 2, 3, 5-tetra-substituted benzene) and 760, 750 cm^{-1} (1, 2-disubstituted benzene); PMR ($CDCl_3$): δ 6.8-7.7 (6H, m, ArH), 2.6-3.3 (4H, m, benzylic), 2.35, 2.56, (6H, $2ArCH_3$), 1.8-2.2 (4H, alicyclic); UV (EtOH): 224, 256; MS: m/z 276 (M^+).

Acid chloride of the acid **3b** (10 g) and anhyd. $AlCl_3$ (5.4 g) in pet. ether (60-80°) were heated on steam-bath for 1 hr to give spiroketone **4b** (5 g). After usual work-up the product was collected at 150-5°/0.3 mm as a light straw coloured liquid with a characteristic odour. Anal. Found: C, 86.39; H, 7.42. Calc. for $C_{20}H_{20}O$: C, 86.95; H, 7.25%. Butyric acid **3c** (3g) under similar conditions and after chromatographic purification (Al_2O_3; pet. ether 60-80°) gave spiroketone **4c** (2g), b.p. 140-45°/0.3 mm as a light yellow coloured liquid. IR (film): 1680 (C=O), 870, 815, 780 cm^{-1}; UV (EtOH): 256 (log ε 4.06), 304 nm (2.87). Anal. Found: C, 87.10; H, 6.79. Calc. for $C_{19}H_{18}O$: C, 86.98; H, 6.91%). Ethyl butyrate **3c** (6g) was stirred with polyphosphoric acid (P_2O_5, 96g; H_3PO_4, 60 mL, 85%) on a steam-bath for 4 hr, and then at 120-30° for 10 min on an oil bath. Usual work-up and chromatographic purification (Al_2O_3, pet. ether 60-80°) gave the spiroketone **4c** (3g), b.p. 140-45°/0.3 mm.

The butyric acid **3d** (2.5 g) as its acid chloride in dry pet. ether (60-80°) under Friedel-Crafts condition gave the spiroketone **4d** (1.8 g), b.p. 140°/0.3 mm; IR (film): 1680 (C=O), 875, 820

cm^{-1}; UV (EtOH): 259 nm (log ε 4.01). Anal. Found: C, 86.78; H, 7.05. Calc. for $C_{20}H_{20}O$: C, 86.92; H, 7.29%. Ethyl butyrate **3d$_E$** (5g) was stirred with polyphosphoric acid (P_2O_5, 70g; H_3PO_4, 50 mL, 85%) under similar conditions of **3c$_E$** gave the spiroketone **4d** (3g), b.p. 140-42°/0.3 mm.

Spiro-ols. In each case, the separate solutions of spiroketones **4a-4d** in dry THF was gradually added to a slurry of LAH in dry THF cooled in ice water. After stirring for 2 hr at room temperature, the mixture was heated under reflux for 6 hr. THF was removed and the reaction mixture worked up as usual to give the corresponding spiro-ols. Spiro-ol **5a** (2.5 g) was obtained from **4a** (3g) after chromatographic purification (silicagel, pet. ether 60-80°); IR (film): 3500-3400, 1040, 880, 760 cm^{-1}. Spiro-ol · **5b** (2g) from **4b** (3.5 g) was collected at 140-45°/0.2 mm as a thick colourless liquid, IR (film): 3450 cm^{-1}. Anal. Found: C, 86.10; H, 6.98. Calc. for $C_{20}H_{22}O$: C, 86.33, H, 7.91%. The compound **4c** (2.8g) gave spiro-ol **5c** (2g) which was collected at 160-65°/0.3 mm as a thick liquid; IR (Nujol): 3390, 1030, 880, 780 cm^{-1}. Compound **5d** (1.2g) obtained from **4d** (2.7g) was collected at 155°/0.2 mm as a thick liquid, IR (film): 3300, 1055, 880, 815 cm^{-1}.

Catalytic dehydrogenation of spiro-compounds. Spiro-compound **5a** (5g) was heated with Pd-C (10%, 0.2g) in a sealed tube at 360-80° for 22 hr. The product was extracted with ether, dried (Na_2SO_4) and the solvent removed. The residual oil was subjected to chromatographic fractionation on basic Al_2O_3 (15 g) using pet. ether (60-80°) as eluant. Each of the third to sixth eluant provided solids which were found to be identical and homogeneous by TLC. These combined solids formed TNB complex in ethanol which on repeated crystallisation from ethanol gave yellow needles, m.p. 158-60°. The regenerated hydrocarbon **6a** from the TNB complex crystallised from ethanol in colourless needles, m.p. 177-78° (lit. 178.5-79°); IR[9] (KBr): 1610, 1500, 1462, 1450, 1380, 1275, 1144, 960, 870, 850, 820, 750 cm^{-1}; PMR ($CDCl_3$): δ 8.46-8.75 (4H, m, ArH), 7.6-8.1 (6H, m, ArH), 2.67 (3H, s, $ArCH_3$), 2.55 (3H, s, $ArCH_3$); UV (EtOH): 320, 306, 294, 268, 258, 225 nm; MS: m/z 256 (M^+).

Under similar conditions, spiro-compound **5b** (1g) afforded an oil (homogeneous on TLC) after chromatography (Al_2O_3, pet. ether 60-80°). It formed TNB complex in ethanol as yellow needles, m.p. 142-44°. The regenerated hydrocarbon, 3-ethylchrysene **6b** crystallised from ethanol as colourless plates, m.p. 112-13° (lit.[10], 113-14°) and TNB complex from regenerated hydrocarbon melted at 143-45° (lit.[10] 145-46°). The subsequent eluates provided small amount of solids which formed TNB complex in methanol as yellow needles, m.p. 189-91°. The regenerated hydrocarbon chrysene crystallised from methanol as colourless leaflets, m.p. 250-52° (lit." 252-54°) and when mixed with authentic pure chrysene showed no depression in m.p. Similarly mixed m.p. of the corresponding TNB complexes showed no depression.

Under similar conditions catalytic dehydrogenation of **5c** (1.5g) gave from the benzene and ether extracts, a viscous oil which on chromatography (Al_2O_3, pet. ether 60-80°) afforded solids (homogeneous by TLC), m.p. 162-63°. It formed picrate in ethanol as orange needles, m.p. 162-63°. The regenerated hydrocarbon, 3-methyl chrysene, crystallised from methanol as colourless leaflets, m.p. 173-74° (lit.[11,12,13] m.p. 173.5-174°); IR (nujol): 1615, 1590, 1260, 1180, 1020, 955, 945, 872, 752, 718 cm^{-1}; PMR ($CDCl_3$): δ 8.72-8.98 (4H, m), 7.60-8.26 (7H, m), 2.63 (3H, s, $ArCH_3$); UV ((EtOH): 340 (log ε 2.24), 325 (3.16), 315 (4.13), 303 (4.16), 295 (3.98), 263 (5.03), 252 (4.89), 224 (4.31); MS: m/z 242 (M^+). Anal. Found: C, 93.90; H, 6.0. Calc. for $C_{19}H_{14}$: C, 94.18; H, 5.78%.

The spiro-compound **5d** (1g) under identical condition of dehydrogenation and extraction with ether and then with benzene gave solids. Chromatography (Al_2O_3, pet ether 60-80°) and repeated crystallisation from ethanol gave 3, 9-dimethyl chrysene as white needles, m.p. 230-31° (lit.[12] 233-5°); IR (nujol): 1600, 1020, 899, 875, 812, 785 cm^{-1}; UV (EtOH): 322, 306, 297, 262, 256, 223 nm; PMR ($CDCl_3$): δ 8.63-8.8 (4H, m), 7.42-8.1 (6H, m), 2.65 (6H, s, $ArCH_3$); MS: m/z 256 (M^+).

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