Reactions of Spiro-indazoles containing Keto-groups. Syntheses of Benz[*a*]aceanthrylenes, Naphth[2,1-*a*]aceanthrylenes, and Fluoranthenes

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Anthrone-10-spiro-3'-3'*H*-indazole (1) and 3*H*-indazole-3-spiro-1'-naphthalen-4'(1'*H*)-one (3), prepared by the cycloaddition of benzyne with 10-diazoanthrone (6) and 4-diazonaphthalen-1(4*H*)-one (7), respectively, thermally rearranged with elimination of nitrogen to 8-hydroxybenz[*a*]aceanthrylene (9b) and 3-hydroxyfluoranthene (11b), respectively. The diazoketone (6) reacted with 1,2-naphthyne to give anthrone-10-spiro-3'-3'*H*-benz[*g*]indazole (4) and anthrone-10-spiro-1'-1'*H*-benz[*e*]indazole (5), which gave the rearrangement product, 10-hydroxynaphth[2,1-*a*]aceanthrylene (12b) by thermolysis. Photolysis of the spiro-indazoles afforded the rearrangement and/or photo-oxidation products. Thermolysis and photolysis are accountable on the basis of formation of biradicals [(14), (18), (19), and (21)] and isomerization of these to fused polycyclic compounds. In particular, the isomerization of the biradical (21) to (12b) involves the formation of the naphtho[*a*]cyclopropene (20).

REACTIONS of benzyne and suitable *p*-diazoketones have been reported to give the compounds (1) and (2), containing both a 3*H*-indazole and a ketone in a spiro-configuration.[1] The system is expected to be highly reactive, because of possibility that biradicals or highly strained benzocyclopropenes might be formed from it by elimination of nitrogen [2-4] and that aromatization of the ketonic portion of the molecule might supply a strong driving force for reactions.[5] However, according to the literature [1] photolysis of the spiro-indazoles (1) and (2) results in loss of nitrogen, but the products have not been identified. We have, therefore, investigated the spiro-indazoles (1) and (3)—(5) from the cycloaddition reactions of arynes and *p*-diazoketones, and found that their thermolysis and photolysis give fused polycyclic compounds.

RESULTS AND DISCUSSION

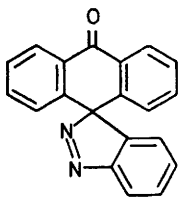
The spiro-indazole (1) was prepared by cycloaddition of the diazoketone (6) to benzyne, generated by aprotic diazotization of anthranilic acid, according to a known method.[1] Similar treatment of the diazoketone (7) with benzyne from the same source afforded the corresponding spiro-indazole (3) in 41% yield. Spectral data of the product are consistent with the proposed structure. The diazoketone (6) reacted with 1,2-naphthyne (generated from 1-amino-2-naphthoic acid) to give the spiro-benzindazoles (4) and (5) in 31 and 9% yields, respectively. The spiro-benzindazoles (4) and (5) were separated by fractional recrystallization, and were differentiated on the basis of their spectra. The n.m.r. spectrum of (5) supports the presence of H-4' of (5).† The isomer ratio observed in the cycloaddition indicates that the direction of the cycloaddition is controlled by electronic and steric factors, and that the cycloaddition is regioselective, the diazo-bearing carbon of the diazoketone (6) predominantly attacking the 2-position of 1,2-naphthyne. The ratio (4) : (5), 31 : 9, is consistent with the data on addition of base to 1,2-naphthyne,[6] and with the greater contribution of (8) to the structure of diazoketones.

† The n.m.r. spectrum of the spiro-indazole (1) showed a one-proton signal (multiplet, δ 8.22—8.35) due to H-7'.

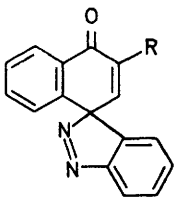
The spiro-indazole (1) readily rearranged in refluxing acetic anhydride with elimination of nitrogen, yielding the acetate (9a) in a 85% yield. Thermolysis of the spiro-indazole (1) in *o*-dichlorobenzene, toluene, or decalin gave the hydroxyaceanthrylene (9b) (51%) [independently by hydrolysis of the acetate (9a)] which was unstable to light and prolonged heating, along with 10-phenylanthrone (10). The products (9a) and (9b) were identified on the basis of their spectral data and chemical behaviour, *i.e.* zinc-dust reduction gave benz[*a*]aceanthrylene (9c). Thermolysis of the spiro-indazole (3) in acetic anhydride afforded the acetate (11a) (94%), thermolysis of which in an inert solvent resulted in 3-hydroxyfluoranthene (11b) (47%). Both the spiro-benzindazoles (4) and (5) in acetic anhydride gave the acetate (12a) almost quantitatively by thermolysis. The expected rearrangement product (13a) from (5) was not obtained, for reasons that will be discussed later. On thermolysis of the spiro-benzindazoles (4) and (5) in a refluxing inert solvent, only 10-hydroxynaphth[2,1-*a*]-aceanthrylene (12b) was obtained. The structures of the rearrangement products (12a) and (12b) were confirmed by their spectral data. In the thermolysis of the spiro-indazoles in an inert solvent, the products (9b), (11b), and (12b) are isolated as the enol rather than the keto-tautomer.[7] However, the product (9b) in solution is in equilibrium with the keto-form. The spiro-indazoles (1) and (3) were converted by zinc-dust reduction into the fused polycyclic hydrocarbons (9c) (49%) and (11c) (64%), respectively. Similar reduction of the spiro-benzindazoles (4) and (5) yielded only the hydrocarbon (12c) (46%). Needless to say, these hydrocarbons were also prepared by reduction of the corresponding rearrangement products.

The thermal rearrangement of the spiro-indazoles (1) and (3)—(5) is at least formally analogous to that of fluorene-9-spiro-3'-3'*H*-indazole to fluoradene [2] and of 3*H*-indazole-3-spiro-1'-indene to 2*H*-cyclopenta[*jk*]-fluorene,[3] and probably involves a biradical process.

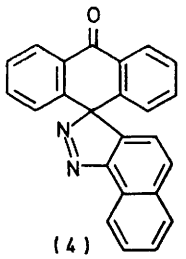
Loss of nitrogen from the spiro-indazole (1) gives the biradical (14), which undergoes biradical cyclization at the 4-position of the anthrone system to give (15), which subsequently isomerizes to (9b). In this reaction the biradical (14) would be expected to abstract hydrogen atoms from the solvent to give 10-phenylanthrone (10), which is obtained, though in very low yield even in solvents such as toluene or decalin. Accordingly it is reasonable that the intramolecular cyclization is much more favourable than the intermolecular reaction, so that the anthrone (10) is not obtained in any appreciable quantity. Thermolysis of the spiro-indazole (1) in benzene containing *N*-phenylmaleimide yielded the adduct (16), presumably derived by capture of the biradical (14). Anthrone-10-spiro-1'-benzocyclopropene (17) may be actually involved in the thermolysis of (1);[4] however, there is no concrete evidence at present relative to this possibility. The thermal rearrangement of the spiro-indazoles (3) and (4) to (11b) and (12b), respectively, is accounted for by pathways involving the formation of the biradicals (18) and (19), by analogy with (1) to (9b). As described above, thermolysis of the spiro-benzindazole (5) gave exclusively the rearrangement product (12b), instead of the expected product (13b). This result undoubtedly indicates that the thermal conversion of (5) to (12b) proceeds by the pathway involving the formation of anthrone-10-spiro-1'-naphtho[*a*]cyclopropene (20). Loss of nitrogen from the spiro-benzindazole (5) leads to the biradical (21), which then cyclizes to the spiro-naphthocyclopropene (20) which in turn gives the biradical (19) by cleavage of the C-10–C-7b bond which then isomerizes to (12b). It is reasonable that the formation of compound (13b) from the biradical (21) may be impossible because of steric hindrance between H-1 and H-14 on compound (13b). A [1,3] sigmatropic pathway from the naphthocyclopropene to the product (12b) is excluded, since a thermal 1,3-antarafacial shift with retention is sterically impossible.



(1)



(2); R = Me
(3); R = H



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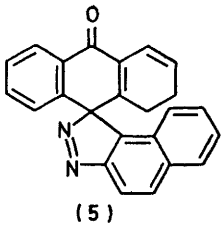

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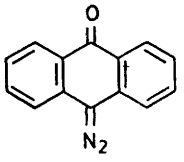

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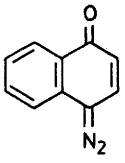

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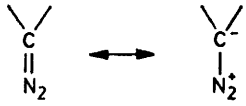

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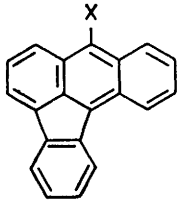

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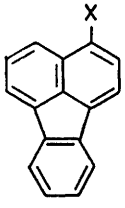

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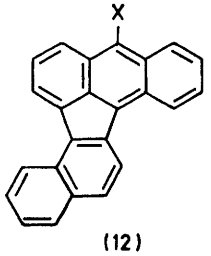

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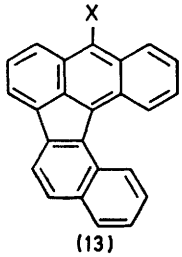
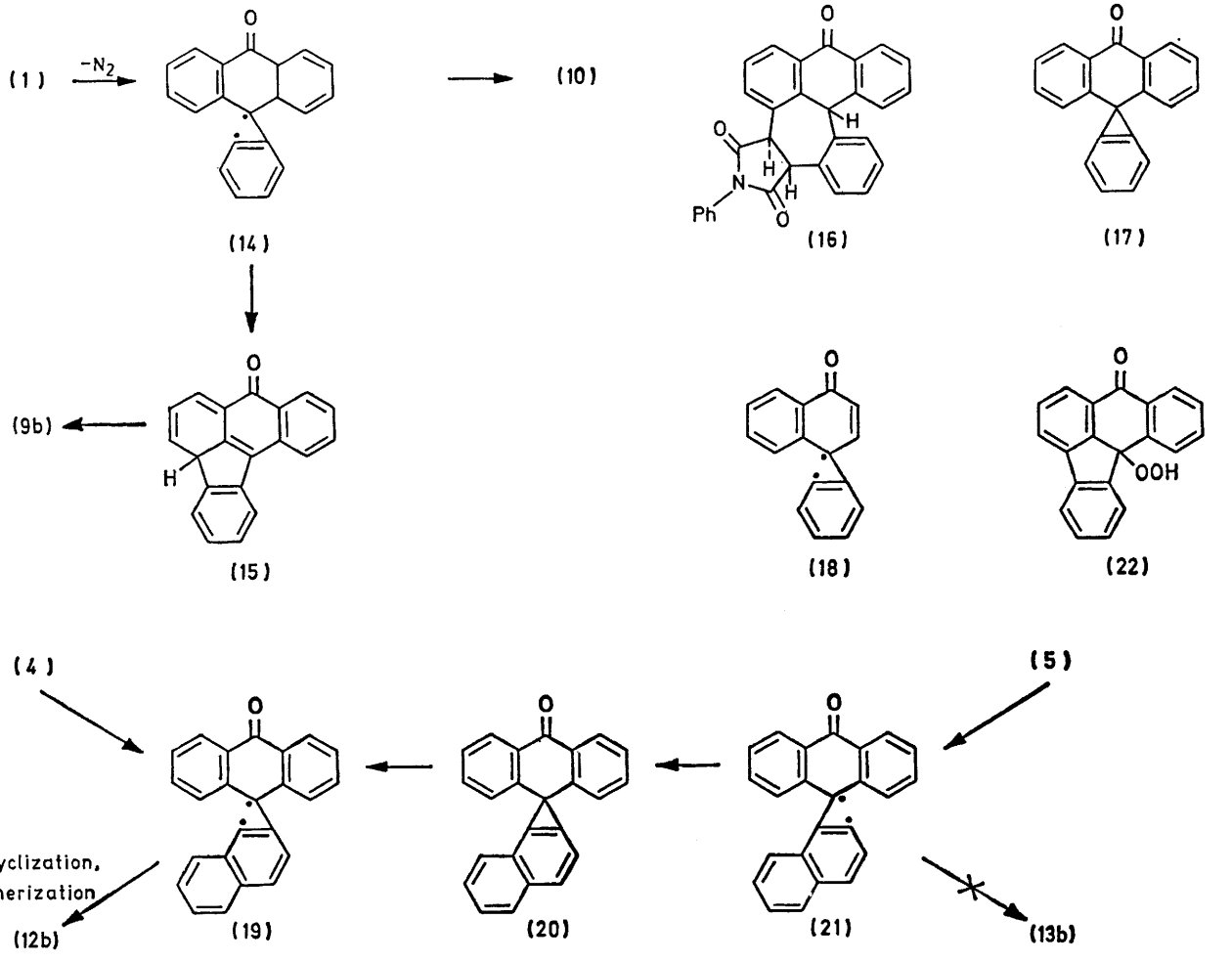


(13)

a; X = OAc, b; X = OH, c; X = H

Irradiation of the spiro-indazole (1) in benzene yielded compound (9b) and a trace amount of 10-phenylanthrone (10). Further prolonged irradiation led to 12b-hydroperoxybenz[*a*]aceanthrylen-8-one (22) (4%) and an unidentified compound (A) (21%). The structural assignment of the hydroperoxide (22) rests on spectral data; elemental and spectral analyses of compound (A) showed that it was an acid of formula $C_{20}H_{12}O_3$. Similar photolysis of (1) in toluene gave a comparable result. On the other hand, photolysis of (1) in isopropyl alcohol afforded compound (A) (20%), 10-hydroxy-10-phenylanthrone (26%), and 10-hydroperoxy-10-phenylanthrone (3%). The formation of these two anthrones can be explained by photo-oxidation of 10-phenylanthrone (10). Photolysis of the spiro-indazoles (3)—(5) in solution (benzene and toluene) gave, as expected, (11b), (12b), and (12b), respectively. Irradi-

ation of the spiro-indazoles [(1) and (3)—(5)] in a matrix of 2-methyltetrahydrofuran at 77 K produced e.s.r. spectra which can be assigned unambiguously to the *biradicals* [(14), (18), (19), and (21)].[2,4,8] In addition to the $\Delta m = 2$ transitions at half-field, six maxima were observed corresponding to the values of the $\Delta m = 1$ transitions (see Experimental section). These results indicate that the photochemical and thermal reactions of the spiro-indazoles are generally similar and that rearrangement of the spiro-indazoles to polycyclic compounds involves biradical a process.



In conclusion, the thermal reactions of these spiro-indazoles are available as a synthetic route to fused polycyclic compounds. The reactions generally go in good yields and there are no by-products to hinder isolation.

EXPERIMENTAL

M.p.s were determined on a Yanagimoto hot-stage apparatus. I.r. spectra were recorded with a JASCO IRA-1 spectrophotometer (KBr disc), n.m.r. spectra with JEOL JNH-3H-60 (60 MHz) and JNH-FX100 (100 MHz) spectrometers for solutions in deuteriochloroform ($SiMe_4$ as internal standard), mass spectra with a JEOL JMS-01SG-2 spectrometer (at 75 eV), and e.s.r. spectra with a JEOL JES-FE-3X spectrometer. Elemental analyses were performed on a Perkin-Elmer model 240 elemental analyser. T.l.c. and column chromatography were carried out on Wakogel B-5 and C-200 (Wako Pure Chemical Industries), respectively. Irradiation were carried out with an Ushio UM102 100-W high-pressure mercury lamp through a Pyrex filter. All known compounds were adequately identified by spectral analyses and t.l.c. The yields reported are based on amounts of isolated products of adequate purity and on amounts of starting materials consumed.

Anthrone-10-spiro-3′-3′H-indazole (1).—The spiro-indazole (1) was prepared by the previously described [1] method from benzyne (generated by treatment of anthranilic acid with isopentyl nitrite) and 10-diazoanthrone.

3H-*Indazole-3-spiro-1′-naphthalen-4′*(1′H)-*one* (3).—A solution of anthranilic acid (3.01 g, 22 mmol) in acetone (40 ml) was added during 1 h to a refluxing solution of 4-diazonaphthalen-1(4*H*)-one (7) [9] (3.40 g, 20 mmol) and isopentyl nitrite (2.57 g, 22 mmol) in dichloromethane (70 ml). After 30 min, the red mixture was filtered and the solvent removed under reduced pressure. Recrystallization of the residue from methanol gave the *spiro-indazole* (3) as colourless microcrystals (2.02 g, 41%), m.p. 118—119 °C (decomp.) (Found: C, 77.8; H, 4.1; N, 11.5. $C_{16}H_{10}N_2O$

requires C, 78.0; H, 4.1; N, 11.4%); $\nu_{max.}$ 1 660 cm^{-1} (CO); δ 6.06 (1 H, d, H-3, *J* 9.8 Hz), 6.15—6.30 (1 H, m, H-5), 6.85 (1 H, d, H-2, *J* 9.8 Hz), 7.15—7.85 (5 H, m, H-6, -7, -4′, -5′, and -6′), and 8.15—8.50 (2 H, m, H-8 and -7′); *m/e* 218 (M^+ — 28, 33%), 189 (100), 187 (21), 163 (23), and 87 (16).

Anthrone-10-spiro-3′-3′H-benz[g]*indazole* (4) *and Anthrone-10-spiro-1′-1′H-benz*[e]*indazole* (5).—A solution of 1-amino-2-naphthoic acid [10] (5.61 g, 30 mmol) in acetone (110 ml) was added dropwise during 1.5 h to a refluxing mixture of 10-diazoanthrone [11] (6.16 g, 28 mmol) and isopentyl nitrite (3.51 g, 30 mmol) in dichloromethane (240 ml). The solvent was removed from the filtrate under reduced pressure at 20—30 °C and the crystalline residue was washed with ethanol and filtered off to give a mixture of the spirobenzindazoles (4) and (5) (6.96 g). Fractional recrystallization of the mixture from acetonitrile afforded the *spirobenzindazole* (4) as colourless microcrystals (2.98 g, 31%), m.p. 135 °C (decomp.) (Found: C, 83.15; H, 4.1; N, 8.2. $C_{24}H_{14}N_2O$ requires C, 83.2; H, 4.1; N, 8.1%); $\nu_{max.}$ 1 655 cm^{-1} (CO); δ 6.20—6.45 (2 H, m, H-4 and -5), 7.12—7.78 (10 H, m, H-2, -3, -6, -7, -4′, -5′, -6′, -7′, -8′, and -9′), and 8.42—8.70 (2 H, m, H-1 and -8); *m/e* 318 (M^+ — 28, 100%), 289 (68), and (287): and then the more soluble *spiro-benzindazole* (5) as colourless columns (0.86 g, 9%), m.p. 155 °C (decomp.) (Found: C, 83.2; H, 4.2; N, 8.2. $C_{24}H_{14}N_2O$ requires C, 83.2; H, 4.1; N, 8.1%); $\nu_{max.}$ 1 660 cm^{-1} (CO); δ 6.09—6.35 (2 H, m, H-4 and -5), 7.07—7.75 (7 H, m, H-2, -3, -6, -7, -5′, -7′, and -8′), 7.96—8.45 (3 H, m, H-4′, -6′, and -9′), and 8.50—8.74 (2 H, m, H-1 and -8); *m/e* 318 (M^+ — 28, 100%), 289 (100), 287 (91), 263 (17), and 261 (18).

Thermolysis of the Spiro-indazole (1).—(a) *In acetic anhydride.* A suspension of the spiro-indazole (1) (1.00 g, 3.38 mmol) in acetic anhydride (50 ml) was refluxed for 2 h. After cooling, the resulting mixture was poured into water. The crystals (1.02 g) which separated were recrystallized from benzene–hexane to give 8-*acetoxybenz*[a]*aceanthrylene* (9a) as yellow microcrystals (0.89 g, 85%), m.p. 189—190 °C (Found: C, 85.0; H, 4.6. $C_{22}H_{14}O_2$ requires C, 85.1; H, 4.55%); $\nu_{max.}$ 1 760 cm^{-1} (CO); δ 2.62 (3 H, s, Me) and 7.20—8.94 (11 H, m, Ar-H); *m/e* 310 (M^+, 10%), 268 (100), 239 (78), and 237 (46).

The acetate (9a) (0.78 g, 2.5 mmol) was dissolved in ethanol–water (95 : 5 v/v) (150 ml) containing sodium hydroxide (2.0 g) and heated at 60—70 °C for 10 min. After cooling, the solution was neutralized with hydrochloric acid and poured into water (500 ml). The reaction was followed by t.l.c., which showed disappearance of the starting material and the formation of a single product. The precipitate was filtered off, and washed with water to afford orange microcrystals of 8-*hydroxybenz*[a]*aceanthrylene* (9b) (0.65 g, 97%), which because of its instability was examined without further treatment; m.p. 120 °C (decomp.) (Found; C, 89.5; H, 4.5. $C_{20}H_{12}O$ requires C, 89.5; H, 4.5%); $\nu_{max.}$ 3 350 cm^{-1} (OH); δ 7.10—8.85 (11 H, m, Ar-H) and 10.86 (1 H, s, OH); *m/e* 268 (M^+, 24%), 267 (100), 238 (40), 236 (15), 119 (13), and 118 (9).

(b) *In o-dichlorobenzene, toluene, or decalin.* A solution of the spiro-indazole (1) (1.00 g, 3.38 mmol) in *o*-dichlorobenzene (100 ml) was refluxed under nitrogen until t.l.c. showed disappearance of the starting material (*ca.* 5 min). T.l.c. analysis of the reaction mixture showed the presence of (9b) and a trace amount of 10-phenylanthrone (10).[12] However, chromatography (benzene as eluant) of the product yielded uncharacterized products, because (9b) is unstable to air, light, and prolonged heating. Therefore, compound (9b) was isolated as the acetate (9a). In a parallel experiment, acetic anhydride (90 ml) was added to the reaction mixture. After stirring at 90 °C for 20 min, the resulting mixture was poured into water and shaken until acetic anhydride was completely hydrolysed. The *o*-dichlorobenzene solution was concentrated and the residue was chromatographed on silica (benzene as eluant) to give the acetate (9a) (0.53 g, 51%). Thermolysis of the spiro-indazole (1) using toluene and decalin as solvent was similar to that described above.

Benz[a]*aceanthrylene* (9c).—To a mixture of the spiro-indazole (1) (1.00 g, 3.38 mmol), zinc dust (1 g), and sodium chloride (1 g) a few drops of water were added, and then the temperature was raised to 200 °C. During 2 h the temperature was allowed to rise to 230 °C, with stirring. After cooling, the reaction mixture was extracted with benzene and the product from the extract was chromatographed on silica (benzene as eluant) to give benz[*a*]-aceanthrylene (9c) as yellow microcrystals (0.35 g, 49%), m.p. 143—144 °C (lit.,[13] 144—145 °C). A similar reduction of (9a) and (9b) yielded the benzaceanthrylene (9c) (50—55%).

Reaction of the Spiro-indazole (1) *with N-Phenylmaleimide.*—A solution of the spiro-indazole (1) (1.00 g, 3.38 mmol) and *N*-phenylmaleimide (1.21 g, 7 mmol) in benzene (500 ml) was heated under reflux until t.l.c. showed the absence of (1) (*ca.* 30 h). The solvent was distilled off, and the residue extracted with hot water; a portion of the *N*-phenylmaleimide was recovered. The residue was chromatographed on silica (benzene as eluant) to afford the *adduct* (16) as colourless microcrystals (0.46 g, 31%), m.p. 213—215 °C (Found: C, 81.6; H, 4.3; N, 3.2. $C_{30}H_{19}NO_3$ requires C, 81.6; H, 4.4; N, 3.2%); $\nu_{max.}$ 1 775 and 1 690 (imide CO), and 1 672 cm^{-1} (anthrone CO); δ 3.08 (1 H, d, *J* 8.0 Hz, CH), 3.53 (1 H, d, *J* 8.0 Hz, CH), 4.80 (1 H, s, Ar_3CH), and 6.40—8.65 (16 H, m, Ar-H); *m/e* 441 (M^+, 4%), 268 (100), 239 (52), 237 (19), and 173 (40).

A photo-reaction of (1) (1.00 g, 3.38 mmol) with *N*-phenylmaleimide (1.21 g, 7 mmol) also gave the adduct (16) (0.12 g, 8%).

The adduct (16) (0.15 g, 0.34 mmol) on refluxing with acetic anhydride (2 h) followed by the usual work-up gave the acetate (9a) (76 mg, 72%).

Thermolysis of the Spiro-indazole (3).—(a) *In acetic anhydride.* Thermolysis of (3) (1.0 g, 4.1 mmol) in acetic anhydride (80 ml) by the procedure described above for (1) yielded 3-acetoxyfluoranthene (11a) as yellow microcrystals (1.0 g, 94%), m.p. 116—117 °C (lit.,[14] 118—119.5 °C).

(b) *In o-dichlorobenzene or decalin.* A solution of the spiro-indazole (3) (1.0 g, 4.1 mmol) in *o*-dichlorobenzene (30 ml) was refluxed until t.l.c. showed disappearance of (3). The solvent was distilled off under reduced pressure and the residue was recrystallized from chloroform to give 3-hydroxyfluoroanthene (11b) as yellow neeedles (0.42 g, 47%), m.p. 186—187 °C (lit.,[14] 187 °C). Thermolysis of (3) using decalin as solvent gave a similar result.

Fluoranthene (11c).—The procedure was similar to that for the preparation of (9c). The product from reduction of the spiro-indazole (3) (1.0 g, 4.1 mmol) was recrystallized from benzene–hexane to give fluoranthene (11c) (0.53 g, 64%), identical with an authentic specimen. A similar reduction of the acetate (11a) at 150 °C for 3 h afforded

(11b) (66%). Further reduction at 240 °C for 2 h gave (11c).

Thermolysis of the Spiro-benzindazoles (4) *and* (5).—(a) *In acetic anhydride.* The procedure employed was similar to that for the reduction of (1). A mixture of the spiro-benzindazole (4) (0.52 g, 1.5 mmol) in acetic anhydride (40 ml) was stirred and heated under reflux for 3 h. After work-up, the product was recrystallized from benzene to give 10-*acetoxynaphth*[2,1-a]*aceanthrylene* (12a) as yellow plates (0.53 g, 98%), m.p. 227—228 °C (Found: C, 86.6; H, 4.5. $C_{26}H_{16}O_2$ requires C, 86.65; H, 4.5%); $\nu_{max.}$ 1 765 cm^{-1} (CO); δ 2.59 (1 H, s, Me) and 7.20—8.75 (13 H, m, Ar-H); *m/e* 360 (M^+, 7%), 318 (100), 317 (91), 289 (96), 287 (82), 285 (29), 261 (16), and 43 (52).

A similar treatment of the spiro-benzindazole (5) in acetic anhydride also gave the acetate (12a) (99%), identical (spectra and mixed m.p.) with the acetate from the spiro-benzindazole (4).

The hydrolysis of the acetate (12a) by the procedure described above for (9a) yielded 10-*hydroxynaphth*[2,1-a]-*aceanthrylene* (12b) as brown microcrystals (96%). Because of its thermal instability it was examined without further treatment; m.p. 111—113 °C (decomp.) (Found: C, 90.4; H, 5.0. $C_{24}H_{14}O$ requires C, 90.5; H, 5.0%); $\nu_{max.}$ 3 200 cm^{-1} (OH); *m/e* 318 (M^+, 30%), 289 (12), 178 (9), 170 (8), 158 (10), 144 (45), 115 (25), and 44 (100).

(b) *In o-dichlorobenzene or decalin.* A solution of the spiro-indazole (4) and (5) (0.52 g, 1.5 mmol) in *o*-dichlorobenzene (50 ml) was refluxed until t.l.c. showed disappearance of the starting material. T.l.c. of the reaction mixture showed only one spot, corresponding to the naphthaceanthrylene (12b). Thermolysis of (4) and (5) using decalin as solvent gave a similar result.

Naphth[2,1-a]*aceanthrylene* (12c).—The procedure was similar to that for the preparation of (9c). The product from reduction of (4) or (5) (0.52 g, 1.5 mmol) was recrystallized from hexane to give red microcrystals of the *naphthaceanthrylene* (12c) (0.21 g, 46%), m.p. 166—167 °C (Found: C, 95.5; H, 4.9. $C_{24}H_{14}$ requires C, 95.3; H, 4.7%); δ 7.43—8.87 (14 H, m, Ar-H); *m/e* 302 (M^+, 100%) and 300 (20). A similar reduction of (12a) and (12b) afforded (12c) (55—60%).

Photolysis of the Spiro-indazole (1).—(a) *In benzene or toluene.* A solution of the spiro-indazole (1) (1.00 g, 3.38 mmol) in benzene (2 l) was irradiated at room temperature for 2 h, during which time the approximately theoretical amount of nitrogen was evolved. T.l.c. of the initial reaction mixture showed the presence of the starting material (1), (9b), and a trace amount of 10-phenylanthrone (10).[12] After irradiation, the resulting solution was concentrated and the residue was chromatographed on silica (benzene as eluant). The first eluate contained an unidentified product (A) (0.21 g, 21%), yellow columns from chloroform, m.p. 150 °C (Found: C, 80.1; H, 4.1. $C_{20}H_{12}O_3$ requires C, 80.0; H, 4.0%); $\nu_{max.}$ 1 718 (acid CO) and 1 622 cm^{-1} (CO); δ 6.50—7.72 (1 H, m, Ar-H) and 12.25 (1 H, s, CO_2H); *m/e* 300 (M^+, 100%), 272 (93), 271 (81), 255 (17), 151 (34), and 121 (38). The second consisted of 12b-*hydroperoxybenz*[a]*aceanthrylen-8-one* (22) (39 mg, 4%), colourless needles from chloroform, m.p. 264—266 °C (decomp.) (Found: C, 80.2; H, 4.2. $C_{20}H_{12}O_3$ requires C, 80.0; H, 4.0%); $\nu_{max.}$ 3 400 (OOH) and 1 660 cm^{-1} (CO); δ 3.45 (1 H, s, OOH) and 7.05—8.35 (11 H, m, Ar-H); *m/e* 300 (M^+, 100%), 284 (95), 283 (80), 271 (17), 255 (17), 226 (27), 215 (19), 213 (18), 189 (14), and 150 (25). Further elution afforded a complex mixture of products which could not be isolated. Similar photolysis in toluene gave a comparable result.

(b) *In isopropyl alcohol.* A solution of the spiro-indazole (1) (1.00 g, 3.38 mmol) in isopropyl alcohol (2 l) was irradiated at room temperature until gas evolution was complete (*ca.* 50 min). The solvent was distilled off, and the residue was chromatographed on silica (benzene as eluant). The first and second eluates contained anthraquinone (17 mg, 2%) and compound (A) (0.20 g, 20%), respectively. The third fraction consisted of 10-*hydroxy*-10-*phenylanthrone* (0.25 g, 26%), colourless columns from chloroform, m.p. 217 °C (Found: C, 83.9; H, 5.0. $C_{20}H_{14}O_2$ requires C, 83.9; H, 4.9%); $\nu_{max.}$ 3 440 (OH) and 1 652 cm^{-1} (CO); δ[$(CD_3)_2CO$] 5.78 (1 H, s, OH), 7.08—7.80 (11 H, m, Ar-H), and 8.12—8.34 (2 H, m, H-1 and -8); *m/e* 286 (M^+, 79%), 268 (26), 257 (8), 239 (17), 209 (100), 152 (62), 105 (26), and 77 (55). The fourth fraction afforded 10-*hydroperoxy*-10-*phenylanthrone* (32 mg, 3%), colourless plates from chloroform, m.p. 177 °C (decomp.) (Found: C, 79.5; H, 4.7. $C_{20}H_{14}O_3$ requires C, 79.45; H, 4.7%); $\nu_{max.}$ 3 330 (OOH) and 1 660 cm^{-1} (CO); δ 1.42 (1 H, s, OOH), 7.01—7.83 (11 H, m, Ar-H), and 8.03—8.43 (2 H, m, H-1 and -8); *m/e* 302 (M^+, 55), 286 (21), 269 (100), 239 (25), 209 (31), and 152 (24).

Photolysis of the Spiro-indazole (3).—A solution of (3) in solvent (benzene or toluene) was irradiated. T.l.c. of the reaction mixture showed only one spot, corresponding to (11b).

Photolysis of the Spiro-benzindazoles (4) *and* (5).—A solution of the spiro-benzindazole (4) or (5) in solvent (benzene or toluene) was irradiated. T.l.c. analysis of the reaction mixture showed only one spot, corresponding to (12b).

E.S.R. Spectra of the Biradicals.—The e.s.r. spectra were obtained upon irradiation of the spiro-indazole in a matrix of 2-methyltetrahydrofuran at 77 K in the cavity of an e.s.r. spectrometer. The e.s.r. spectrum of the biradical (14) obtained from photolysis of (1) revealed six maxima corresponding to the values of the $\Delta m = 1$ transition (the zero-field splitting parameters are $D = 0.051\ 9$, $E = 0.005\ 9\ cm^{-1}$).[8] At half field (1 636 G, $\Delta m = 2$ transitions, $\nu = 9.230$ GHz), intense absorption was observed. Similarly the e.s.r. spectrum of the biradical (18) from (3) exhibited absorptions due to $\Delta m = 1$ transitions ($D = 0.046\ 1$, $E = 0.004\ 0\ cm^{-1}$) and $\Delta m = 2$ transitions (1 625 G, $\nu = 9.209$ GHz). In the cases of the spiro-benzindazoles (4) and (5), in addition to the spectrum of the biradical (19) or (21), the spectrum[15] corresponding to a triplet from the naphthalene portion of the spiro-benzindazole was observed. The data of the spectra of the biradicals (19) and (21), respectively: $D = 0.051\ 3$, $0.054\ 0\ cm^{-1}$; $E = 0.006\ 1$, $0.005\ 9\ cm^{-1}$ ($\Delta m = 1$); 1 613, 1 611 and 1 609 G * ($\Delta m = 2$, $\nu = 9.206$ GHz). All g values ($\Delta m = 1$) are close to 2.002.

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* This probably is due to conformational isomerism of the biradical (28).

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