Syntheses and Reactions of Spirocyclopropaneanthrones. Part 2.[1] Rearrangements and Cyclopropyl Ring-opening Reactions of Phenyl-substituted Spirocyclopropaneanthrones and Related Compounds

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Diphenylspirocyclopropaneanthrones [(1c) and (1d)] thermally rearranged with ring expansion to 1,10b-dihydro-2*H*-aceanthrones (2), whereas the phenyl analogue (1b) did not rearrange under comparable conditions. Phenylspirocyclopropeneanthrone (3a), prepared by the carbenic reaction of 10-diazoanthrone (6) with phenylacetylene, thermally rearranged to 10b*H*-aceanthrone (11). By contrast, the diphenyl analogue (3b), from the reaction with diphenylacetylene, was thermally stable. The diazoketone (6) reacted with 9-methylenefluorene to give directly the rearrangement product (2g), instead of the dispirocyclopropaneanthrone (1g). Spirocyclopropane- and spirocyclopropene-anthrones [(1) and (3)] reacted under acidic conditions to yield cyclopropyl or cyclopropenyl ring-opened products. In these reactions, the ring was shown to open from the more substituted side. These reactions are discussed in mechanistic terms.

In the context of our investigations [1-3] on the reactions of spiro-compounds having a quinone moiety, we have further examined related compounds. We have previously shown that dispiro[anthrone-10,1'-cyclopropane-2',10''-anthrone] (1a) thermally rearranged with ring expansion to 1,10b-dihydrospiro[2*H*-aceanthrone-2,10'-anthrone] (2a).[1] This work has now been extended to the reactions of spiro- and dispiro-cyclopropaneanthrones [(2b)—(2g)] and spirocyclopropene analogues (3) to investigate their reactivity in this rearrangement.

These spirocyclopropane- and spirocyclopropene-anthrone systems were also expected to be highly reactive, not only because of the high degree of strain in the cyclopropane or cyclopropene ring, but also because of the possibility that aromatization of the quinone portion of the molecule might supply a strong driving force to reaction. In addition, these systems are intriguing in that protonation of the carbonyl oxygen may lead to a hydroxy-carbocation which could conceivably be bridged, as shown in (4) or (5).[4] We also studied the reactions of the carbocations (4) and (5).

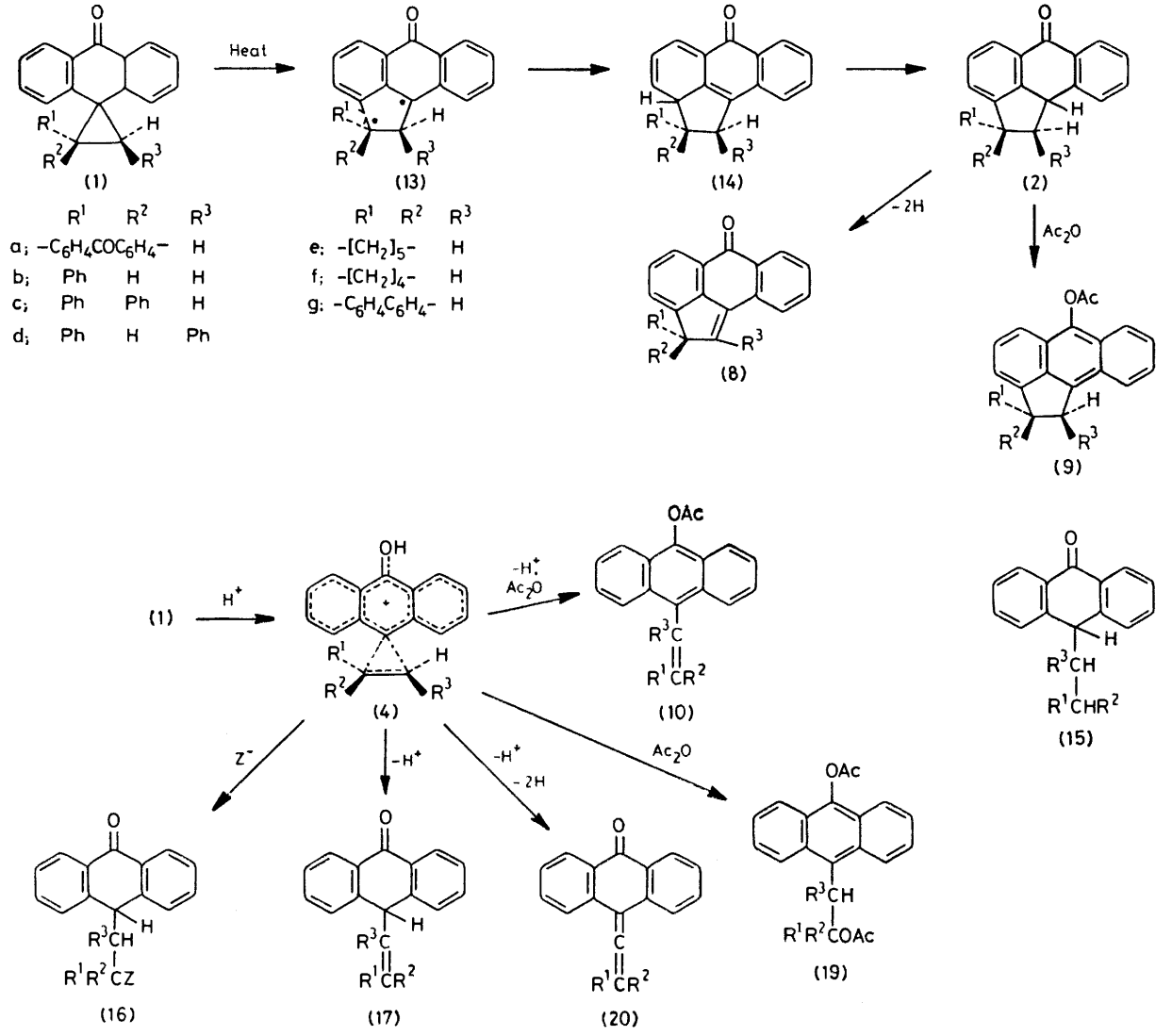
RESULTS AND DISCUSSION

The phenyl-substituted spirocyclopropaneanthrones [(1b)—(1d)] were prepared by irradiation of 10-diazoanthrone (6) in benzene containing the corresponding ethylenes according to a known method.[5] The dispirocycloproaneanthrones [(1e) and (1f)] were obtained from similar photoreactions of the diazoketone (6) with methylenecycloalkanes. The structures of (1e) and (1f) were confirmed by their spectral data and the following observations. Their oxidation with chromium trioxide afforded only anthraquinone, and their zinc-dust reduction in acetic anhydride led to 10-acetoxy-9-cycloalkylmethylanthracenes [(7e) and (7f)]. The phenyl-substituted spirocyclopropeneanthrone [(3a) and (3b)] were also obtained by similar treatment of the diazoketone (5) with phenylacetylenes. The structures of (3a) and (3b) were identified on the basis of their spectral data and chemical behaviour (see their acid-induced ring-opening reactions and reductive acetylation shown below). However, the thermal reactions of the diazoketone (6) with 9-methylenefluorene and of diazofluorene with 10-methyleneanthrone gave the rearrangement product, spiro-[2*H*-aceanthrone-2,9'-fluorene] (8g) in 6 and 41% yields, respectively, instead of the desired dispirocyclopropaneanthrone (1g). In the case of the photoreactions, neither (8g) nor (1g) was obtained. The structural assignment of the 2*H*-aceanthrone (8g) rests on its spectral data and chemical behaviour, *i.e.* its reductive acetylation leading to 6-acetoxyspiro[aceanthrone-2,9'-fluorene] (9g).

Thermal Rearrangement.—Several spirocyclopropane- and spirocyclopropene-anthrones having phenyl groups on their cyclopropane or cyclopropene ring, and dispirocyclopropaneanthrones, rearranged thermally to the intended products. Heating of the spirocyclopropaneanthrone (1c) in refluxing acetic anhydride gave 6-acetoxy-2,2-diphenylaceanthrene (9c) (65%); treatment in refluxing xylene led to 2,2-diphenyl-2*H*-aceanthrone (8c) (41%), which gave the aceanthrene (9c) 87%) by reductive acetylation with zinc dust in acetic anhydride. The spectral data of (9c) is consistent with the proposed structure. Similarly, the spirocyclopropaneanthrone (1d) in refluxing acetic anhydride gave 6-acetoxy-*trans*-1,2-diphenylaceanthrene (9d) (53%), whose structure was substantiated by n.m.r. spectra, showing two doublets for H-1 and -2 at δ 5.15 and 4.75 ($J_{1,2}$ 3.5 Hz), respectively. Thermolysis of (1d) without solvent afforded 1,10b-dihydro-*trans*-1,2-diphenyl-2*H*-aceanthrone (2d) and 1,2-diphenyl-2*H*-aceanthrone (8d) in 32 and 18% yields, respectively. Acetylation of (2d) led to (9d); reductive acetylation of (8d) gave 6-acetoxy-*cis*-1,2-

diphenylaceanthrene (90%), the structure of which followed from n.m.r. spectral data [two doublets for H-1 and -2 at δ 5.60 and 5.35 ($J_{1,2}$ 8.2 Hz), respectively]. The 1,10b-dihydro-2*H*-aceanthrones (2) could not be isolated previously owing to their reactivity, and even under a nitrogen atmosphere attempts to isolate them led to the 2*H*-aceanthrone (8).[1] In the case of (1d), the product (2d) was isolated as the keto-tautomer rather than as the enol tautomer. Treatment of the spirocyclopropaneanthrone (1b) in refluxing acetic anhydride–pyridine resulted in formation of the ring-opened product, 10-acetoxy-9-*trans*-styrylanthracene (10b) (51%), whereas treatment in only acetic anhydride gave no reaction. Thermolysis of dispirocyclopropaneanthrones [(1e) and (1f)] in an inert solvent, and without solvent, gave spiro-[2*H*-aceanthrone-2,1′-cyclohexane] (8e) and the cyclopentane analogue (8f) in 29 and 37% yields, respectively; a complex product mixture resulted from the reaction in refluxing acetic anhydride. Treatment of the spirocyclopropeneanthrone (3a) in acetic anhydride and in inert solvent gave 2-phenyl-10b*H*-aceanthrone (11a) (86%) and 6-acetoxy-2-phenylaceanthrylene (12a) (83%), respectively; however, (3b) was thermally stable and similar treatment gave no reaction. The structural assignments for (11a) and (12a) are based on their spectral data.

Mechanistically, this thermal rearrangement with ring



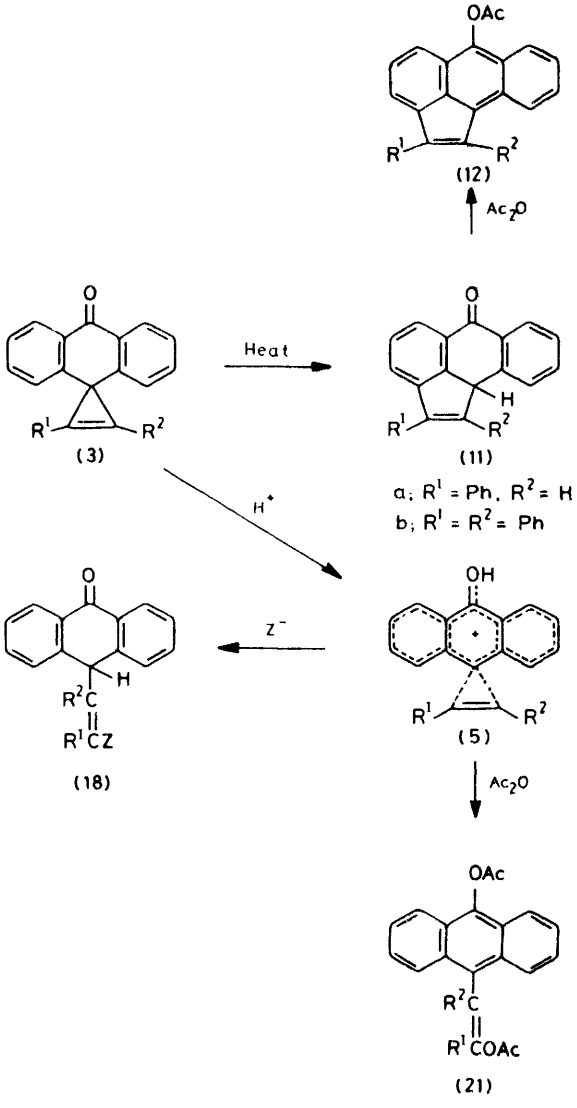
	R^1	R^2	R^3
a;	$-C_6H_4COC_6H_4-$		H
b;	Ph	H	H
c;	Ph	Ph	H
d;	Ph	H	Ph

	R^1	R^2	R^3
e;	$-[CH_2]_5-$		H
f;	$-[CH_2]_4-$		H
g;	$-C_6H_4C_6H_4-$		H

than as the enol tautomer. Treatment of the spirocyclopropaneanthrone (1b) in refluxing acetic anhydride–pyridine resulted in formation of the ring-opened product, 10-acetoxy-9-*trans*-styrylanthracene (10b) (51%), whereas treatment in only acetic anhydride gave no reaction. Thermolysis of dispirocyclopropaneanthrones [(1e) and (1f)] in an inert solvent, and without solvent, gave spiro-[2*H*-aceanthrone-2,1′-cyclohexane] (8e) and the cyclopentane analogue (8f) in 29 and 37% yields, respectively; a complex product mixture resulted from the reaction in refluxing acetic anhydride. Treatment of the spirocyclopropeneanthrone (3a) in acetic anhydride and in inert solvent gave 2-phenyl-10b*H*-aceanthrone (11a) (86%) and 6-acetoxy-2-phenylaceanthrylene (12a) (83%), respectively; however, (3b) was thermally stable and similar treatment gave no reaction. The structural assignments for (11a) and (12a) are based on their spectral data.

Mechanistically, this thermal rearrangement with ring expansion is formally analogous to that of the spirocyclopropanefluorenes to cyclopenta[*jk*]fluorene[6] and of spiroanthroneindazoles to benz[*a*]aceanthrylenes.[2] In addition, such rearrangements do not occur by acid catalysts (see section on acid-induced ring-opening reactions), and do not proceed by a sigmatropic pathway since a thermal 1,3-antarafacial shift with retention is sterically impossible. Therefore, the rearrangement of the spirocyclopropaneanthrones (1) probably involves the following biradical pathway: cyclopropyl ring cleavage at the C-10–C-2′ bond, *i.e.* from the more sub-

stituted side to generate the more stable biradical (13), the cyclization to the intermediate (14), and isomerization to (2). In this rearrangement reaction, the biradical (13) would be expected to abstract hydrogen from



solvent or intermediate species to give compound (15) or its acetate (in acetic anhydride), which was not detected in any of the thermal reaction products. Further, e.s.r. spectroscopy failed to detect the presence of the biradical. However, it is reasonable that the intramolecular cyclization of (13) to (14) is much more favourable than the intermolecular reaction, so that (15) is not produced, and also that the cyclization proceeds too fast to detect the biradical e.s.r. signal under thermal reaction conditions. Retention of stereochemistry upon rearrangement of (1c) to (2c) or (9c) [the two phenyl groups of (1c), (2c), and (9c) are *trans*], supports the idea that the intramolecular cyclization of the biradical (13) is fast. Similarly, the rearrangement of cyclopropene analogue (3) is accounted for by the biradical pathway.

Acid-induced Ring-opening Reactions.—The reactions of the spirocyclopropaneanthrones [(1b)—(1d)] and the spirocyclopropene analogue (3) with acidic reagent (Hz) were expected to give the ring-opened products (16) and (17), and (18),[7] respectively. These reactions are analogous to those of spirocyclopropanecyclohexadienones under acidic conditions.[8] However, the ring-opened products of the types [(16)—(18)] were too unstable to be isolated, and were oxidized by atmospheric oxygen to form anthraquinone during work-up. It was possible to stabilize the products by acetylation with acetic anhydride. Therefore, the acid-induced reactions of (1) and (3) were carried out in acetic anhydride containing a small amount of sulphuric acid. The acid-induced reaction of the spirocyclopropaneanthrone (1a) at room temperature gave the diacetoxyphenylethylanthracene (19b) (26%), but at 95 °C led to the acetoxystyrylanthracene (10b) (71%), which was also prepared independently by reductive acetylation of the spirocyclopropeneanthrone (3a) in 83% yield. The acid-induced reaction of the spirocyclopropaneanthrone (1c) at room temperature gave the acetoxydiphenylvinylanthracene (10c) (63%) and 10-(2,2-diphenylvinylidene)-anthrone (20c) (10%). The cumulene (20c) was also obtained in 58% yield by the reaction of (1c) in acetic acid containing sulphuric acid. The structure of (20c) was confirmed by direct comparison with an authentic sample prepared independently by dehydration of 10-(2,2-diphenylvinyl)-10-hydroxyanthrone.[9] The similar reactions of (1d) and (3b) afforded the anthracene (10d) (75%), which was prepared by reductive acetylation of (3b), and the anthracene (21b) (32%). The spectral data of these anthracenes are consistent with the proposed structures. On the other hand, a complex product mixture resulted from the acid-induced reactions of (1e), (1f), and (3a). Thus, several spirocyclopropane- and spirocyclopropene-anthrones under acidic conditions undergo the cyclopropyl and cyclopropenyl ring-opening, respectively, at the more substituted side. This direction of ring-opening is consistent with our expections that the cleavage would be controlled by the stability of the cationic centre. The acid-induced reactions may be rationalized by postulating protonation on the oxygen atom of the carbonyl group to form the hydroxy-carbocations (4) and (5),[4] which then react with an available nucleophile, or undergo elimination of hydrogen on the less substituted cyclopropyl carbon, followed by acetylation of the 10-hydroxy-group with acetic anhydride. In the acid-induced reaction of the spirocyclopropanes (1), the competition between the reaction with a nucleophile and elimination of a proton in (4) is compatible with the general results expected between S_N1 and $E1$ reactions; *i.e.* elimination becomes favoured over reactions with a nucleophile when reaction temperatures are elevated or when cyclopropyl carbons are more phenyl-substituted.

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 (tetramethylsilane as internal standard), and mass spectra with a JEOL JMS-01SG-2 spectrometer (at 75 eV). Elemental analyses were performed on a Coleman model 33 carbon–hydrogen analyser. T.l.c. and column chromatography were carried out on Wakogel B-5 and C-200 (Wako Pure Chemical Industries), respectively. Irradiations were carried out with an Ushio UM102 100-W high-pressure mercury lamp through a Pyrex filter.

The following compounds were prepared according to reported methods: 2′-phenyl-, 2′,2′-diphenyl-, and *trans*-2′,3′,diphenyl-spiro[anthrone-10,1′-cyclopropane] [(1b), (1c), and (1d)].[5]

Dispiro[*anthrone*-10,1′-*cyclopropane*-2′,1″-*cyclohexane*] (1e).—A solution of 10-diazoanthrone (6) [10] (1.10 g, 5 mmol) and methylenecyclohexane [11] (0.48 g, 5 mmol) in benzene (100 ml) was irradiated at room temperature under nitrogen for 3 h, during which time the approximately theoretical amount of nitrogen was evolved. The resulting solution was concentrated, and the residue was chromatographed on silica (benzene as eluant). The first eluate gave the *dispirocyclopropaneanthrone* (1e) as colourless plates (0.33 g, 23%), m.p. 185—186 °C (decomp.) (Found: C, 87.3; H, 7.1. $C_{21}H_{20}O$ requires C, 87.5; H, 7.0%); $\nu_{max.}$ 1 660 cm^{-1} (CO); δ 0.60—1.55 (10 H, m, C_5H_{10}), 1.91 (2 H, s, CH_2), 7.05—7.75 (6 H, m, Ar-H), and 7.95—8.30 (2 H, m, H-1 and -8); *m/e* 288 (M^+, 91%), 206 (100), 194 (65), 178 (98), and 165 (29). The second and third fractions contained anthraquinone (10%) and 10,10′-bianthrone (27%), respectively, identical with authentic specimens.[12]

Dispiro[*anthrone*-10,1′-*cyclopropane*-2′,1″-*cyclopentane*] (1f).—A solution of the diazoketone (6) (1.10 g, 5 mmol) and methylenecyclopentane [13] (0.42 g, 5 mmol) in benzene (100 ml) was irradiated under nitrogen until gas evolution was complete. The mixture was chromatographed to give the *dispirocyclopropaneanthrone* (1f) as colourless plates (0.18 g, 13%), m.p. 155—157 °C (decomp.) (Found: C, 87.5; H, 6.55. $C_{20}H_{18}O$ requires C, 87.6; H, 6.6%); $\nu_{max.}$ 1 638 cm^{-1} (CO); δ 0.70—1.80 (8 H, m, C_4H_8), 2.22 (2 H, s, CH_2), 6.95—7.50 (6 H, m, Ar-H), and 7.85—8.10 (2 H, m, H-1 and -8); *m/e* 274 (M^+, 51%), 206 (77), 194 (100), 178 (48), and 165 (37).

2′-*Phenylspiro*[*anthrone*-10,1′-*cyclopropene*] (3a).—A solution of the diazoketone (6) (0.55 g, 2.5 mmol) and phenylacetylene (3.83 g, 37.5 mmol) in benzene (100 ml) was irradiated under nitrogen until t.l.c. showed disappearance of the diazoketone (6) (1 h). The solvent was removed from the filtrate under reduced pressure at 20—30 °C, and the residue was then chromatographed on silica (benzene as eluant). The first eluate contained unchanged phenylacetylene. The second fraction was recrystallized from hexane–benzene to give the *spirocyclopropeneanthrone* (3a) as yellow microcrystals (0.35 g, 48%), m.p. 118—124 °C (decomp.) (Found: C, 89.6; H, 4.8. $C_{22}H_{14}O$ requires C, 89.8; H, 4.8%); $\nu_{max.}$ 1 640 cm^{-1} (CO); δ 7.06 (1 H, s, H-3′), 7.15—7.55 (11 H, m, Ar-H), and 8.35—8.70 (2 H, m, H-1 and -8); *m/e* 294 (M^+, 89%), 265 (100), 263 (53), 239 (24), 189 (27), 187 (17), and 163 (16).

2′,3′-*Diphenylspiro*[*anthrone*-10,1′-*cyclopropene*] (3b).—A solution of the diazoketone (6) (0.55 g, 2.5 mmol) and diphenylacetylene (6.68 g, 37.5 mmol) in benzene (100 ml) was irradiated under nitrogen until t.l.c. showed disappearance of (6) (2 h), and the resulting mixture was chromatographed on silica (benzene as eluant). The first fraction consisted of unchanged diphenylacetylene. The second fraction contained the *spirocyclopropeneanthrone* (3b) (0.19 g, 21%) as colourless microcrystals, m.p. 275—277 °C (Found: C, 90.5; H, 5.0. $C_{28}H_{18}O$ requires C, 90.8; H, 4.9%); $\nu_{max.}$ 1 645 cm^{-1} (CO); δ 7.20—7.70 (16 H, m, Ar-H) and 8.45—8.75 (2 H, m, H-1 and -8); *m/e* 370 (M^+, 100%), 341 (24), 339 (33), 293 (62), 265 (35), 263 (32), and 163 (17).

Spiro-[2H-*acenanthrone*-2,9′-*fluorene*] (8g).—A solution of 10-methyleneanthrone [14] (2.60 g, 10 mmol) and 9-diazofluorene [15] (1.92 g, 10 mmol) in xylene (50 ml) was refluxed until t.l.c. showed the absence of the diazofluorene (3 h), and the products were then chromatographed on silica. The first and second eluates (benzene–hexane, 1 : 1) contained 9,9′-bifluorenylidene (0.31 g, 19%) and fluorenone azine (0.01 g, 0.6%), respectively, identical with authentic specimens.[16] The third (benzene) afforded the *spiroaceanthrone* (8g) as yellow microcrystals (1.49 g, 41%), m.p. 223—224 °C (Found: C, 91.2; H, 4.5. $C_{28}H_{16}O$ requires C, 91.3; H, 4.4%); $\nu_{max.}$ 1 638 cm^{-1} (CO); δ 6.58—8.50 (16 H, m, Ar-H and H-1); *m/e* 368 (M^+, 100%), 339 (48), and 337 (18).

A similar reaction of 10-methyleneanthrone with 9-diazofluorene using refluxing benzene as solvent gave the spiroaceanthrone (8g) (6%), 9,9′-bifluorenylidene (46%), and fluorenone azine (1%). The spiroaceanthrone (8g) was prepared in a 9% yield by the thermal reaction of 10-diazoantbrone (6) with 9-methylenefluorene,[17] freshly prepared, in refluxing toluene. Neither the spiroaceanthrone (8g) nor the dispirocyclopropaneanthrone (1g) was obtained on photoreaction, either of 9-diazofluorene with 10-methyleneanthrone or of 10-diazoanthrone (6) with 9-methylenefluorene.

Reductive Acetylation of the Spirocyclopropaneanthrones (1e) *and* (1f).—A mixture of (1e) (0.43 g, 1.5 mmol) and zinc dust (5 g) in acetic anhydride (30 ml) was kept at room temperature for 50 h. The resulting mixture was filtered, and the filtrate was poured into water; the precipitate was chromatographed on silica. The first eluate (benzene) contained 10-*acetoxy*-9-(*cyclohexylmethyl*)*anthracene* (7e) (0.21 g, 42%) as light yellow needles, m.p. 149—150 °C (Found: C, 83.05; H, 7.4. $C_{23}H_{24}O_2$ requires C, 83.1; H, 7.3%); $\nu_{max.}$ 1 752 cm^{-1} (CO); δ 0.85—2.05 (11 H, m, C_6H_{11}), 2.63 (3 H, s, Me), 3.50 (2 H, d, CH_2), and 7.10—8.25 (8 H, m, Ar-H); *m/e* 332 (M^+, 18%), 290 (69), 207 (100), 194 (60), and 149 (73). The second fraction (chloroform) consisted of 9,10-diacetoxyanthracene (25%), identical with an authentic specimen.

A similar reductive acetylation of (1f) gave 10-*acetoxy*-9-(*cyclopentylmethyl*)*anthracene* (7f) (47%) as light yellow needles, m.p. 162—163 °C (Found: C, 83.0; H, 7.1. $C_{22}H_{22}O_2$ requires C, 83.0; H, 7.0%); $\nu_{max.}$ 1 760 cm^{-1} (CO); δ 1.10—1.80 (9 H, m, C_5H_9), 2.05 (3 H, s, Me), 3.57 (2 H, d, CH_2), and 7.25—8.45 (8 H, m, Ar-H); *m/e* 318 (M^+, 21%), 276 (72), 207 (100), 178 (24), and 43 (17): and then 9,10-diacetoxyanthracene (12%).

Reductive Acetylation of the Spiroaceanthrone (8g).—A mixture of (8g) (0.37 g, 1 mmol) and zinc dust (5 g) in acetic anhydride (30 ml) was stirred and heated under reflux for 3 h. After the usual work-up, the product was chromatographed on silica (benzene as eluant) to give, besides

identified minor products, 6-*acetoxyspiro*[*aceanthrene*-2,9'-*fluorene*] (9g) (0.18 g, 44%) as yellow microcrystals, m.p. 230—231 °C (Found: C, 87.35; H, 4.95. $C_{30}H_{20}O_2$ requires C, 87.35; H, 4.9%); $\nu_{max.}$ 1 754 cm^{-1} (CO); δ 2.63 (3 H, s, Me), 4.26 (2 H, s, CH_2), and 6.35—8.15 (15 H, m, Ar-H); *m/e* 412 (M^+, 18%), 370 (100), 339 (36), 207 (14), 149 (14), and 43 (36).

Thermal Reactions of the Spirocyclopropane- and Spirocyclopropene-anthrones (1) and (3). *General Procedures.*—(a) *In acetic anhydride.* A solution of a spiroanthrone (1–5 mmol) in acetic anhydride (20 ml) was heated under reflux until t.l.c. showed disappearance of the starting spiroanthrone (2—10 h). After cooling, the resulting mixture was poured into water. The crystals which had formed were collected and worked up by an appropriate method.

(b) *In acetic anhydride–pyridine.* Procedure (b) was identical with (a) except that pyridine (2 ml) was added to a solution of a spiroanthrone in acetic anhydride.

(c) *In an inert solvent.* A solution of a spiroanthrone (1 mmol) in benzene or xylene (30 ml) was refluxed until t.l.c. showed disappearance of the spiroanthrone (1—4 h). The solvent was distilled off, and the residue was worked up by an appropriate method.

(d) *Without solvent.* A spiroanthrone (1 mmol) was heated without solvent at its melting point. After 1 min, the product was worked up by an appropriate method.

(i) 2'-*Phenylspiro*[*anthrone*-10,1'-*cyclopropane*] (1b). The product from (1b) (1.48 g, 5 mmol) by procedure (b) was recrystallized from benzene–hexane to give 10-*acetoxy*-9-*styrylanthracene* (10b) as yellow microcrystals (0.86 g, 51%), m.p. 209 °C (Found: C, 85.4; H, 5.47. $C_{24}H_{18}O_2$ requires C, 85.2; H, 5.4%); $\nu_{max.}$ 1 773 cm^{-1} (CO); δ 2.55 (3 H, s, Me), 6.79 (1 H, d, *J* 16.5 Hz, vinyl H), 7.75 (1 H, d, *J* 16.5 Hz, vinyl H), and 7.15—8.50 (13 H, m, Ar-H); *m/e* 338 (M^+, 18%), 296 (50), 295 (47), 265 (21), 217 (14), 189 (14), and 43 (100).

Treatment of (1b) by procedure (a) gave no reaction. Thermolysis of (1b) by procedures (c) or (d) afforded a complex mixture.

(ii) 2',2'-*Diphenylspiro*[*anthrone*-10,1'-*cyclopropane*] (1c). The product from (1c) (0.37 g, 1 mmol) by procedure (a) was recrystallized from benzene–hexane to give 6-*acetoxy*-2,2-*diphenylaceanthrene* (9c) as yellow plates (0.27 g, 65%), m.p. 219—220 °C (Found: C, 86.8; H, 5.4. $C_{30}H_{22}O_2$ requires C, 86.9; H, 5.35%); $\nu_{max.}$ 1 762 cm^{-1} (CO); δ 2.58 (3 H, s, Me), 4.52 (2 H, s, CH_2), and 7.05—8.25 (17 H, m, Ar-H); *m/e* 414 (M^+, 91%), 372 (100), 371 (47), 295 (64), 294 (47), 293 (46), 265 (62), 263 (33), and 43 (19). The thermal reaction of (1c) by procedure (b) was similar to that described above.

The product mixture from (1c) (0.37 g, 1 mmol) in xylene by procedure (c) was chromatographed on silica (benzene as eluant) to give 2,2-*diphenyl*-2H-*aceanthrone* (8c) as yellow microcrystals (0.17 g, 41%), m.p. 224—225 °C (Found: C, 90.8; H, 5.0. $C_{28}H_{18}O$ requires C, 90.8; H, 4.9%); $\nu_{max.}$ 1 658 cm^{-1} (CO); δ 7.05—8.65 (18 H, m, Ar-H and H-1); *m/e* 370 (M^+, 100%), 341 (21), 339 (24), 293 (76), 265 (29), 263 (30), and 43 (19).

A mixture of the aceanthrone (8c) (0.37 g, 1 mmol) and zinc dust (6 g) in acetic anhydride (30 ml) was stirred and refluxed for 2 h. After the usual work-up, chromatography [benzene–hexane (3 : 1) as eluant] of the product gave the aceanthrene (9c) (0.36 g, 87%), identical with an authentic specimen from thermal reaction of (1c) in acetic anhydride.

(iii) trans-2',3'-*Diphenylspiro*[*anthrone*-10,1'-*cyclopropane*] (1d). The product from (1d) (0.37 g, 1 mmol) by procedure (a) was recrystallized from benzene–hexane to give 6-*acetoxy*-trans-1,2-*diphenylaceanthrene* (9d) as light yellow microcrystals (0.22 g, 53%), m.p. 200—202 °C (Found: C, 86.7; H, 5.35. $C_{30}H_{22}O_2$ requires C, 86.9; H, 5.35%); $\nu_{max.}$ 1 770 cm^{-1} (CO); δ 2.63 (3 H, s, Me), 4.75 (1 H, d, *J* 3.5 Hz, H-2), 5.15 (1 H, d, *J* 3.5 Hz, H-1), and 6.85—8.25 (17 H, m, Ar-H); *m/e* 414 (M^+, 21%), 372 (83), 371 (41), 294 (54), 293 (80), 265 (76), 263 (63), and 43 (100).

The product from (1d) (0.37 g, 1 mmol) by procedure (d) was chromatographed on silica (benzene as eluant). The first eluate contained 1,10b-*dihydro*-1,2-*diphenyl*-2H-*aceanthrone* (2d) (0.12 g, 32%) as yellow microcrystals (from benzene–hexane), m.p. 177—178 °C (Found: C, 90.3; H, 5.4. $C_{28}H_{20}O$ requires C, 90.3; H, 5.4%); $\nu_{max.}$ 1 662 cm^{-1} (CO); δ 3.66 (1 H, t, *J* 10.8 Hz, H-1), 4.56 (1 H, d, *J* 10.8 Hz, CH), 4.85 (1 H, d, *J* 10.8 Hz, CH), 6.80—7.50 (15 H, m, Ar-H), and 7.90—8.95 (2 H, m, H-5 and -7); *m/e* 372 (M^+, 47%), 370 (43), 294 (100), 293 (51), 265 (83), 263 (60), 252 (23), 78 (56), and 77 (62). The second fraction consisted of 1,2-diphenyl-2*H*-aceanthrone (8d) (67 mg, 18%), m.p. 195—198 °C (Found: C, 90.8; H, 4.9. $C_{28}H_{18}O$ requires C, 90.6; H, 5.0%); $\nu_{max.}$ 1 640 cm^{-1} (CO); δ 5.12 (1 H, s, H-2), 6.75—7.80 (15 H, m, Ar-H), and 7.90—8.65 (2 H, m, H-5 and -7); *m/e* 370 (M^+, 100%), 293 (45), 265 (30), 263 (45), and 77 (25).

The dihydroaceanthrone (2d) (0.19 g, 0.51 mmol) on warming with acetic anhydride (20 ml) and sodium acetate (1 g) on a steam-bath (4h) followed by the usual work-up gave the acetoxyaceanthrene (9d) (0.19 g, 90%), identical with an authentic specimen from thermal reaction of (1d) in acetic anhydride.

A mixture of the aceanthrone (8d) (0.19 g, 0.51 mmol) and zinc dust (2 g) in acetic anhydride (20 ml) was stirred and refluxed for 4 h. After the usual work-up, the product was chromatographed on silica (benzene as eluant) to give 6-*acetoxy*-cis-1,2-*diphenylaceanthrene* as light yellow microcrystals (0.10 g, 47%), m.p. 245—247 °C (Found: C, 86.85; H, 5.3. $C_{30}H_{22}O_2$ requires C, 86.9; H, 5.35%); $\nu_{max.}$ 1 765 cm^{-1} (CO); δ 2.63 (3 H, s, Me), 5.35 (1 H, d, *J* 8.2 Hz, H-2), 5.60 (1 H, d, *J* 8.2 Hz, H-1), and 6.40—8.25 (17 H, m, Ar-H); *m/e* 414 (M^+, 7%), 372 (37), 371 (17), 294 (29), 293 (49), 265 (46), 263 (44), and 43 (100).

(iv) *Dispiro*[*anthrone*-10,1'-*cyclopropane*-2',1''-*cyclohexane*] (1e). The product mixture from (1e) (0.29 g, 1 mmol) by procedure (d) was chromatographed on silica (benzene as eluant) to give anthraquinone (63 mg, 30%) and *spiro*-[2H-*aceanthrone*-2,1'-*cyclohexane*] (8e) as yellow plates (83 mg, 29%), m.p. 169—170 °C (Found: C, 88.1; H, 6.3%. $C_{21}H_{18}O$ requires C, 88.1; H, 6.3%); $\nu_{max.}$ 1 630 cm^{-1} (CO); δ 1.8 (10 H, m, C_5H_{10}) and 7.10—8.20 (8 H, m, Ar-H and H-1); *m/e* 286 (M^+, 100%), 257 (33), 244 (99), 243 (30), 231 (29), 230 (20), and 202 (18). N.m.r. and g.l.c. analyses of the crude product mixture showed the presence of methylenecyclohexane (13%). The product from (1e) in xylene by procedure (c) was comparable to that described above. A complex mixture resulted from the treatment of (1e) by procedures (a) or (b).

(v) *Dispiro*[*anthrone*-10,1'-*cyclopropane*-2',1''-*cyclopentane*] (1f). The product from (1f) (0.27 g, 1 mmol) by procedure (d) was chromatographed (benzene as eluant) to give anthraquinone (6 mg, 4%) and *spiro*-[2H-*aceanthrone*-2,1'-*cyclopentane*] (8f) as light yellow plates (0.10 g, 37%), m.p. 126—128 °C (Found: C, 88.1; H, 5.9. $C_{20}H_{16}O$

requires C, 88.2; H, 5.9%); $\nu_{max.}$ 1 642 cm^{-1} (CO); δ 2.06 (8 H, m, C_4H_8) and 7.20—8.65 (8 H, m, Ar-H and H-1); *m/e* 272 (M^+, 100%), 244 (97), 243 (50), 231 (35), 230 (36), 215 (53), 213 (21), 202 (66), and 189 (23).

(vi) 2′-*Phenylspiro*[*anthrone*-10,1′-*cyclopropene*] (3a). The product from (3a) (0.29 g, 1 mmol) by procedure (a) was recrystallized from chloroform–hexane to give 6-*acetoxy*-2-*phenylaceanthrylene* (12a) as yellow needles (0.28 g, 83%), m.p. 176—178 °C (Found: C, 85.5; H, 4.85. $C_{24}H_{16}O_2$ requires C, 85.7; H, 4.8%); $\nu_{max.}$ 1 762 cm^{-1} (CO); δ 2.59 (3 H, s, Me) and 7.15—8.40 (13 H, m, Ar-H and H-1); *m/e* 336 (M^+, 3%), 294 (31), 293 (31), 265 (23), 263 (35), 261 (12), 239 (12), 237 (9), and 43 (100).

The product from (3a) (0.29 g, 1 mmol) in benzene by procedure (c) was recrystallized from benzene–hexane to give 2-*phenyl*-10bH-*aceanthrone* (11a) as yellow microcrystals (0.2 g, 86%), m.p. 147—149 °C (Found: C, 89.6; H, 4.9. $C_{22}H_{14}O$ requires C, 89.8; H, 4.8%); $\nu_{max.}$ 1 644 cm^{-1} (CO); δ 4.98 (1 H, d, H-10b) and 6.95—8.60 (13 H, m, Ar-H and H-1); *m/e* 294 (M^+, 100%), 265 (72), 263 (45), 239 (41), 237 (19), 217 (30), 189 (96), 187 (74), and 163 (30).

The aceanthrone (11a) (0.15 g, 0.51 mmol) on warming with acetic anhydride (20 ml) containing sodium acetate (1 g) on a steam-bath (1 h) followed by the usual work-up gave the aceanthrylene (12a) (0.15 g, 88%), identical with an authentic specimen from thermal reaction of (3a) in acetic anhydride.

(vii) 2′,3′-*Diphenylspiro*[*anthrone*-10,1′-*cyclopropene*] (3b). Treatment of (3b) by procedures (a)—(c) gave no reaction. Thermolysis of (3b) by procedure (d) afforded a complex product mixture.

Acid-induced Ring-opening Reactions in Acetic Anhydride. General Procedure.—A solution of a spiroanthrone (1—2 mmol) in acetic anhydride (30 ml) containing sulphuric acid (0.5 ml) was allowed to stand at room temperature or at 95 °C. After t.l.c. showed disappearance of the starting spiroanthrone, the reaction mixture was poured into water. The precipitate was collected and worked up by an appropriate method.

(i) *Spirocyclopropaneanthrone* (1b). The product from the reaction (at room temperature for 24 h) of (1b) (0.59 g, 2 mmol) was chromatographed on silica (benzene as eluant) to give 10-*acetoxy*-9-(2-*acetoxy*-2-*phenylethyl*)*anthracene* (19b) as yellow microcrystals (0.21 g, 26%), m.p. 128—129 °C (decomp.) (Found: C, 78.6; H, 5.7. $C_{26}H_{22}O_4$ requires C, 78.4; H, 5.6%); $\nu_{max.}$ 1 773 and 1 735 cm^{-1} (CO); δ 1.83 (3 H, s, Me), 2.58 (3 H, s, Me), 3.89 (1 H, dd, J_{AB} 14.2, J_{AX} 6.2 Hz, H_A of $CH_XCH_AH_B$), 4.19 (1 H, dd, J_{AB} 14.2, J_{BX} 8.1 Hz, H_B of $CH_XCH_AH_B$), 6.13 (1 H, dd, J_{AX} 6.2, J_{BX} 8.1 Hz, H_X of $CH_XCH_AH_B$), and 7.05—8.45 (13 H, m, Ar-H); *m/e* 398 (M^+, 12%), 356 (15), 296 (13), 207 (100), and 43 (64).

The product from the reaction of (1b) (0.59 g, 2 mmol) at 95 °C for 2 h was recrystallized to give the acetoxystyrylanthracene (10b) (0.48 g, 71%). The anthracene (10b) was also prepared independently from the following experiment. A mixture of the spirocyclopropeneanthrone (3a) (0.29 g, 1 mmol) and zinc dust (2 g) in acetic anhydride (20 ml) was stirred and refluxed for 30 min. After the usual work-up, the product was recrystallized to give the anthracene (10b) (0.28 g, 83%).

(ii) *Spirocyclopropaneanthrone* (1c). The product from the reaction (at room temperature for 2 h) of (1c) (0.37 g, 1 mmol) was chromatographed (benzene as eluant). Fractional recrystallization of the first eluate afforded 10-*acetoxy*-9-(2,2-*diphenylvinyl*)*anthracene* (10c) as yellow microcrystals (0.26 g, 63%), m.p. 235 °C (Found: C, 86.9; H, 5.4. $C_{30}H_{22}O_2$ requires C, 86.9; H, 5.4%); $\nu_{max.}$ 1 770 cm^{-1} (CO); δ 2.52 (3 H, s, Me) and 7.70—8 45 (19 H, m, vinyl and Ar-H); *m/e* 414 (M^+, 69%), 372 (100), 371 (58), 339 (11), 295 (33), 294 (32), 293 (42), 265 (47), 263 (17), and 43 (38): and 10-(2,2-*diphenylvinylidene*)*anthracene* (20c) as colourless needles (37 mg, 10%), m.p. 227—228 °C (lit.,[9] 220 °C), identical with an authentic specimen prepared by dehydration of 10-(2,2-diphenylvinyl)-10-hydroxyanthrone.[9]

The cumulene (20c) was prepared independently by the following experiment. A solution of the spirocyclopropaneanthrone (1c) (0.74 g, 2 mmol) in acetic acid (30 ml) containing sulphuric acid (1 ml) was stirred at room temperature for 1 day. The resulting mixture was poured in water, and then the precipitate was chromatographed on silica (benzene as eluant) to give the cumulene (20c) (0.43 g, 58%).

(iii) *Spirocyclopropaneanthrone* (1d). The product from the reaction (at room temperature for 4 h) of (1d) (0.37 g, 1 mmol) was recrystallized from benzene–hexane to give 10-*acetoxy*-9-(1,2-*diphenylvinyl*)*anthracene* (10d) as light yellow microcrystals (0.31 g, 75%), m.p. 202 °C (Found: C, 86.8; H, 5.35. $C_{30}H_{22}O_2$ requires C, 86.8; H, 5.4%); $\nu_{max.}$ 1 775 cm^{-1} (CO); δ 2.57 (3 H, s, Me) and 6.45—8.20 (19 H, m, vinyl and Ar-H); *m/e* 414 (M^+, 10%), 372 (53), 371 (33), 339 (16), 295 (30), 294 (32), 293 (33), 265 (73), 263 (47), and 43 (100). The anthracene (10d) was obtained by reductive acetylation of the spirocyclopropeneanthrone (3b) (32%). The procedure employed was similar to that for reductive acetylation of the spirocyclopropeneanthrone (3a).

(iv) *Spirocyclopropeneanthrone* (3b). The product from the reaction (at room temperature for 1 h) of (3b) (0.37 g, 1 mmol) was chromatographed on silica (benzene as eluant) to give 10-*acetoxy*-9-(2-*acetoxy*-1,2-*diphenylvinyl*)*anthracene* (21b) as yellow microcrystals (0.15 g, 32%), m.p. 208—210 °C (Found: C, 81.2; H, 5.2. $C_{32}H_{24}O_4$ requires C, 81.3; H, 5.1%); $\nu_{max.}$ 1 770 cm^{-1} (CO); δ 2.18 (3 H, s, Me), 2.62 (3 H, s, Me), and 6.80—8.65 (18 H, m, Ar-H); *m/e* 472 (M^+, 79%), 430 (90), 388 (100), 387 (53), 370 (91), 283 (55), 281 (32), 252 (32), 105 (67), 78 (38), 77 (42), and 43 (31).

Reaction of the dispirocyclopropaneanthrones (1e) and (1f), and the spirocyclopropeneanthrone (3a), under acidic conditions afforded a complex mixture which led to anthraquinone during work-up.

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