636. *The Tropylium Ion. Part V.*[1] *Synthesis of Cyclopropa*[l]-*phenanthrene Derivatives and Attempted Formation of the Dibenzo*-[a,c]*tropylium Cation.*

By M. J. S. Dewar and C. R. Ganellin.

With ethyl diazoacetate phenanthrene gives a 1,2-adduct in addition to the 9,10-adduct previously reported. The Hunsdiecker reaction with the silver salt (II; R = CO_2Ag) gives the iodide (II; R = I), together with a monoester of 9-phenanthrylmethanediol. Curtius rearrangement of the azide (II; R = $CO{\cdot}N_3$), followed by hydrolysis, gives the amine which, on diazotisation in concentrated hydrochloric acid, furnishes the chloride. Attempts to prepare the dibenzo[*a,c*]tropylium cation indicate that this ion is less stable than predicted.

The tropylium cation together with its benzologues provides a valuable opportunity for correlating experimental observation with predictions given by LCAO-MO theory. The p*K* values and the frequency of the first (long-wave) light-absorption bands of these cations have been calculated by Heilbronner and his collaborators.[2] Of this series, the 2,3-naphthotropylium and the dibenzo[*a,c*]tropylium (I) cation have not yet been prepared. The most promising route to the latter appeared to be by way of 5,5a-dihydro-4b*H*-cyclopropa[*l*]phenanthrene-5-carboxylic acid (dibenzonorcaradienecarboxylic acid) (II; R = CO_2H) which we hoped to convert into the cation (I) by one of the methods described in our previous publications.[1,3]

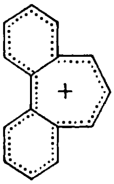
---

[1] Part IV, *J.*, 1959, 2438.

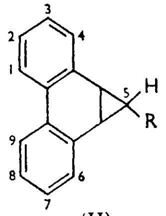
[2] Heilbronner, Meuche, and Strauss, *Helv. Chim. Acta*, 1958, **41**, 57, 414.

[3] Dewar and Pettit, *J.*, 1956, 2021, 2026.

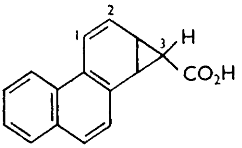
The preparation of the acid (II; R = CO_2H) by the reaction of ethyl diazoacetate with phenanthrene was described by Drake and Sweeney[4] and confirmed by Cook, Dickson, and Loudon,[5] but neither group of investigators recorded the yield of purified product. On repeating this reaction we obtained a 50% yield of crude product, from which only a 6% yield of the desired acid (m. p. 256°) could be isolated. We also obtained an equal amount of an isomeric acid (III) (m. p. 180°). The latter readily added one mol. of bromine and was easily oxidised by permanganate, indicating the presence of a localised ethylenic bond and excluding the possibility that phenanthrene had undergone substitution by ethyl diazoacetate to give a phenanthrylacetic ester. The light absorption of the acid (III) (Fig. 1) resembled that of α-vinylnaphthalene but showed extended conjugation. These results suggest that the acid was 3,3a-dihydro-2b*H*-cyclopropa[*a*]phenanthrene-3-carboxylic acid (III). Thus ethyl diazoacetate reacts with both the 9,10- and the 1,2-bond in phenanthrene and in this case cannot be considered as a selective " double-bond " reagent as defined by Badger.[6] Presumably reaction at the 3,4-bond is sterically hindered, and reaction is unfavourable at the 2,3-bond since this would produce an *ortho*-quinonoid structure.



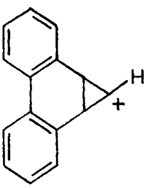
(I)



(II)



(III)



(IV)

Treatment of the silver salt of acid (I) with bromine, as in the normal Hunsdiecker reaction, did not produce the bromide (II; R = Br); instead, bromination of the phenanthrene nucleus occurred. A similar reaction with iodine was more successful but gave a mixture of the iodide (II; R = I) and an ester (A). Unfortunately, these could only be separated by a tedious fractional crystallisation and this limited their availability. Chromatography, on alumina or silica gel with a variety of solvents, was unsuccessful and chemical methods failed owing to the instability of their derivatives.

In contrast to tropylium iodide, the iodide (II; R = I) was readily soluble in organic solvents of low polarity and insoluble in aqueous acids, indicating that the covalent structure was dominant. It was not ionised even in 98% sulphuric acid, and addition of silver perchlorate to this solution resulted in oxidation. The iodide did react with silver perchlorate in dry nitromethane, producing silver iodide and a deep yellow solution; addition of dry ether to this solution removed the colour but failed to precipitate the expected dibenzotropylium salt, and evaporation gave a tar. These results indicated that dibenzotropylium perchlorate was formed in solution, giving rise to the observed yellow colour, but that it was too unstable to be isolated under these conditions.

The action of concentrated sulphuric acid on carboxylic acids $R{\cdot}CO_2H$ results in decomposition to R^+ if this is a stable ion;[7] *e.g.*, triphenylacetic acid gives carbon monoxide, water, and triphenylmethyl hydrogen sulphate. While the light absorption of the acid (II; R = CO_2H) in 98% sulphuric acid (Fig. 2) was very different from that in ethanol (Fig. 1), the expected long-wave band of the dibenzotropylium cation was absent and the acid rapidly underwent sulphonation.

Decarbonylation of the acid chloride (II; R = COCl) with silver perchlorate, in contrast to a similar reaction of cyclohepta-2,4,6-trienecarbonyl chloride,[1] did not lead to the desired cation but gave oxidation products.

---

[4] Drake and Sweeney, *J. Org. Chem.*, 1946, **11**, 67.

[5] Cook, Dickson, and Loudon, *J.*, 1947, 746.

[6] Badger, *Quart. Rev.*, 1951, **5**, 147.

[7] Gillespie and Leisten, *ibid.*, 1954, **8**, 40.

Since we had not been able to isolate a salt of the cation (I), we tried to prepare the alcohol (II; R = OH). This should rearrange in the presence of strong acids to the dibenzotropylium cation. The iodide (II; R = I) was easily hydrolysed; it gave a precipitate with silver nitrate in warm ethanol. Unfortunately, with sodium hydroxide it gave a mixture of acids. Attempts to convert the iodide into the acetate (II; R = OAc) failed. In a further attempt the acid (II; R = CO_2H) was converted, *via* the acid chloride, into the azide and then into the isocyanate (II; R = NCO) by a Curtius rearrangement. Acid-hydrolysis of the isocyanate gave the amine hydrochloride (II; R = NH_2,HCl). Diazotisation of this amine in dilute mineral acid gave polymeric material and none of the expected alcohol, and in concentrated hydrochloric acid the chloride (II; R = Cl) was produced. These results are very similar to those described by Pettit in the cyclopropa-acenaphthene series.[8]

The chloride (II; R = Cl), in contrast to the iodide, gave no reaction with alcoholic silver nitrate. The comparative ease with which the iodide was hydrolysed was therefore due to the weakness of the C–I bond and not to a tendency for the halide to ionise. Although the chloride appeared to be inert, when treated with aluminium chloride in nitromethane it gave a deep green solution, and addition of a trace of water destroyed the colour; however, the equivalent conductance of solutions of these two compounds in nitrobenzene did not indicate significant interaction. The chloride did not react with acetyl fluoroborate, antimony pentachloride, silver acetate, or silver perchlorate. These results are in contrast to the successful formation of the dibenzo[*a,e*]tropylium [9] and the perinaphthindenylium [8] cation from their corresponding covalent chlorides.

FIG. 1. *Ultraviolet spectra of the acid* (II; R = CO_2H) (——), *and* (III) (- - - -), *in ethanol.*

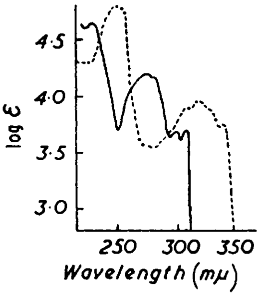
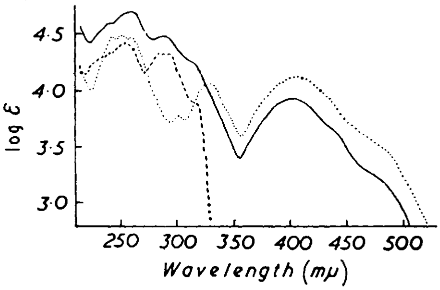


FIG. 2. *Ultraviolet spectra of the α-hydroxy-9-phenanthrylmethyl ester of the acid* (II; R = CO_2H) (——) *the acid* (II; R = CO_2H) (- - - -), *and phenanthrene-9-aldehyde* (. . . .), *in* 98% *sulphuric acid.*



As already described, the Hunsdiecker reaction with iodine gave an ester (A) in addition to the expected iodide. A well-established product from this type of reaction is the ester between the starting acid and the next lower alcohol, *i.e.*, that formed by the Simonini reaction.[10] Hydrolysis of the ester (A) gave the acid (II; R = CO_2H), but the alcoholic constituent was not isolated. Esters, in general, undergo solvolysis in sulphuric acid, ionisation occurring with alkyl–oxygen fission:[11] $R'{\cdot}CO{\cdot}O{-}\vdots{-}R + H_2SO_4 \longrightarrow R'{\cdot}CO_2H + R^+HSO_4^-$. The ester (A) dissolved in concentrated sulphuric acid with immediate production of a bright yellow colour and we assumed at first that this was due to the formation of the dibenzotropylium cation. However, dilution of this solution gave phenanthrene-9-aldehyde instead of the expected 2,3:4,5-dibenzocyclohepta-2,4,6-trienol (the base expected to be formed on hydrolysis of the cation). The aldehyde gave a yellow solution in 98% sulphuric acid and had a visible absorption identical with that of the

---

[8] Pettit, *Chem. and Ind.*, 1956, 1306.
[9] Berti, *Gazzetta*, 1957, **87**, 293.
[10] Johnson and Ingham, *Chem. Rev.*, 1956, **56**, 219.
[11] Kuhn, *J. Amer. Chem. Soc.*, 1949, **71**, 1575.

ester (A) (Fig. 2). Analysis of the ester (A) agreed with the formula (II; R = $CO{\cdot}O{\cdot}C_{15}H_{11}O$) and indicated that it was the half ester of 9-dihydroxymethylphenanthrene. It is likely that the carbonium ion (IV) is initially formed in the Hunsdiecker reaction and that this rearranges with autoxidation before esterification. A similar cationic intermediate has been demonstrated in the reaction of silver cyclobutanecarboxylate with iodine whereby cyclopropylmethyl cyclobutanecarboxylate is the major product.[12]

The difficulty encountered in preparing the dibenzo[*a,c*]tropylium cation indicates that it is less stable than predicted. The tribenzo[*a,c,e*]tropylium cation [13] is also much less stable than predicted and a common feature of these two cations is the resistance to planarity of the seven-membered ring, and therefore to effective overlap of adjacent *p*-orbitals, arising from steric interference of the *o*-hydrogen atoms; the LCAO-MO calculations neglect the effect of configurational interaction. The failure to prepare the alcohol (II; R = OH) in the above experiments suggests that this too is unstable.

EXPERIMENTAL

Microanalyses were carried out by the microanalytical laboratory of the Imperial College of Science and Technology, London. Ultraviolet absorption spectra were determined with a Unicam S.P. 500 spectrophotometer.

Addition of Ethyl Diazoacetate to Phenanthrene.—Ethyl diazoacetate (180 g.) was added dropwise with stirring to liquid phenanthrene (1040 g.) at 155—165°. The addition was controlled to give a steady evolution of nitrogen and required 6 hr. Heating was continued for a further 1 hr. and *ca.* 34 l. of nitrogen were collected. The hot mixture was then refluxed with potassium hydroxide (90 g.) in ethanol (3 l.) for 3½ hr. and poured into water (6 l.); the precipitated phenanthrene was filtered off from the cold solution and washed with 2N-sodium hydroxide (200 ml.). The washings were combined with the main filtrate, then extracted with ether (2 × 500 ml.) to remove traces of phenanthrene and evaporated under reduced pressure to half the volume. Acidification of this solution with concentrated hydrochloric acid gave the product as a sticky precipitate which became granular after a few hours and was then filtered off and dried (yield, 185 g., 50%).

The crude acid was stirred with boiling benzene (400 ml.) and the mixture was filtered while hot. The residue was fractionally crystallised (" triangular method ") from dioxan and gave the acid (II; R = CO_2H) as needles (22 g., 5·9%), m. p. 255—256·5° (Found: C, 81·5; H, 5·3. Calc. for $C_{16}H_{12}O_2$: C, 81·3; H, 5·1%)

Partial evaporation of the benzene filtrate afforded a solid which was recrystallised several times from benzene, to give 3,3a-*dihydro*-2bH-*cyclopropa*[a]*phenanthrene*-3-*carboxylic acid* as prisms (23·5 g., 6·3%), m. p. 180—181° [Found: C, 81·7; H, 5·4%; equiv., 239; *M* (Rast), 236. $C_{16}H_{12}O_2$ requires C, 81·3; H, 5·1%; equiv., and *M*, 236]. A solution of this acid in benzene readily reacted with bromine to give a pale yellow solid which could not be crystallised since in warm benzene hydrogen bromide was evolved and a yellow resin remained.

Similar results were obtained on addition of ethyl diazoacetate under the conditions described by Drake and Sweeney,[4] *viz.*, at a lower temperature, with a lower concentration of ethyl diazoacetate, and for a longer time.

Hunsdiecker Reaction.—The acid (II; R = CO_2H) was neutralised with warm 0·2N-sodium hydroxide, and an equivalent amount of aqueous silver nitrate was added. The white precipitate of the silver salt was filtered off and washed with water, then acetone, partially dried at 100° for 30 min., and finally dried *in vacuo* over phosphoric oxide (yield 97%).

(*a*) Bromine (3·1 g., 0·0194 mole) was added dropwise with stirring to a suspension of the silver salt (6·7 g., 0·0196 mole) in dry, refluxing carbon tetrachloride (750 ml.). No carbon dioxide was evolved. Refluxing was continued for 2½ hr. The mixture was filtered from the precipitate of silver bromide, extracted with 2N-sodium hydroxide (2 × 70 ml.) and evaporated, leaving a polymeric residue. The alkaline extracts, together with some sodium salt which had been precipitated, were acidified and the resulting precipitate was filtered off, dried, and crystallised from benzene to give white needles of x-*bromo*-5,5*a*-*dihydro*-4bH-*cyclopropa*[l]*phenanthrene*-5-*carboxylic acid* (3·5 g., 58%), m. p. 271—273° (decomp. 274°) (Found:

---

[12] Roberts and Simmons, *J. Amer. Chem. Soc.*, 1951, **73**, 5487.

[13] Stiles and Libbey, *J. Org. Chem.*, 1957, **22**, 1243.

C, 60·8; H, 3·8; Br, 24·9. $C_{16}H_{11}O_2Br$ requires C, 61·0; H, 3·5; Br, 25·4%), $\lambda_{max.}$ (in ethanol) 224, 276—282, 307, 315 mμ (log ε 4·62, 4·20, 3·89, 3·87 respectively).

(*b*) The silver salt (19·1 g., 0·056 mole) was added to a solution of resublimed iodine (14·2 g., 0·056 mole) in dry benzene (900 ml.) at 0°; the mixture was stirred for 1½ hr. at 0°, then refluxed for 2½ hr. during which carbon dioxide was evolved. The precipitated silver iodide was then filtered off and dried (12·8 g., 98%). The benzene filtrate was extracted with 2N-sodium hydroxide (2 × 100 ml.), and these extracts together with some sodium salt which had been precipitated were acidified to give the acid (II; R = CO_2H) (4·2 g., 32%). Evaporation of the benzene solution gave two products (8·3 g.) in nearly equal amounts which were separated by fractional crystallisation from benzene. 5,5a-*Dihydro*-5-*iodo*-4bH-*cyclopropa*[l]*phenanthrene*, which was the less soluble, crystallised as pale yellow prisms, m. p. 140° (decomp.) (Found: C, 56·4; H, 3·6; I, 40·6. $C_{15}H_{11}I$ requires C, 56·6; H, 3·5; I, 39·9%), $\lambda_{max.}$ (in chloroform) 256—268 mμ (log ε 4·05). The other component, which crystallised as needles, was α-*hydroxy*-9-*phenanthrylmethyl* 5,5a-*dihydro*-4bH-*cyclopropa*[l]*phenanthrene*-5-*carboxylate*, m. p. 238—239° (Found: C, 84·2; H, 5·0. $C_{31}H_{22}O_3$ requires C, 84·0; H, 5·0%), $\lambda_{max.}$ (in chloroform) 256, 268—271 (infl.), 274—277 (infl.), 298, 309·5, 330, 337, 345 mμ (log ε 4·67, 4·41, 4·39, 4·15, 3·87, 2·30, 2·14, 2·06 respectively).

Hydrolysis of the ester (140 mg.) by refluxing benzene (20 ml.) and 4N-sulphuric acid (30 ml.) for 2 hr. gave the acid (II; R = CO_2H) (77 mg.), identified by its ultraviolet light absorption and mixed m. p.

Treatment of the ester (110 mg.) for 5 min. with 98% sulphuric acid (2 ml.) gave a deep yellow solution. This was poured on ice (20 g.), and the precipitate was filtered off and washed with warm 2N-sodium hydroxide. Crystallisation of the residue from light petroleum (b. p. 60—80°) gave 9-phenanthrenealdehyde (10 mg.), m. p. 100—101°, having ultraviolet and infrared spectra identical with those of material prepared by Dornfeld and Coleman's method.[14]

Silver perchlorate (0·20 g.) in dry nitromethane (2 ml.) was added to a solution of the iodide (0·17 g.) in dry toluene (3 ml.), and the mixture was heated at 80° for 5 min. in nitrogen. The resulting precipitate of silver iodide was filtered off under nitrogen, and dry ether (from sodium) was added to the deep yellow filtrate. Although the colour had been destroyed no salt was precipitated; evaporation gave a green polymer. The effect of traces of moisture rendered it impossible to measure the light absorption of the above yellow filtrate.

Treatment of the Acid (II; R = CO_2H) *with Sulphuric Acid*.—The acid (0·41 g.) with 98% sulphuric acid (3 ml.) gave a green solution. After 10 min. this was poured on ice (10 g.), and the precipitate was filtered off. Crystallisation from benzene containing a few drops of ethanol gave needles, m. p. 157—159° (decomp.). This product was very hygroscopic and gave an acidic solution in water; it contained sulphur but did not give consistent analyses. In ethanol it had $\lambda_{max.}$ 228, 276, 286, 301, 313 mμ (log ε 4·41, 4·16, 4·16, 3·80, 3·79 respectively).

5,5a-*Dihydro*-4bH-*cyclopenta*[l]*phenanthrene*-5-*carboxylic Anhydride*.—When the acid chloride (II; R = COCl) (see below) was treated with pyridine, as in the procedure of Allen *et al.*[15] for *p*-chlorobenzoic anhydride, the *anhydride* was obtained; it crystallised from benzene as needles, m. p. 233—234° (90%) (Found: C, 84·5; H, 5·2. $C_{32}H_{22}O_3$ requires: C, 84·7; H, 4·9%), $\lambda_{max.}$ (in chloroform) 251, 272, 281, 297, 310 mμ (log ε 4·68, 4·52, 4·51, 4·15, 4·08 respectively).

Curtius Reaction.—The acid (II; R = CO_2H) (15 g.) was refluxed for 1½ hr. with thionyl chloride (10 g.) in benzene (100 ml.) containing 6 drops of pyridine. The solution was decanted from pyridine hydrochloride and evaporated. The residue of acid chloride crystallised from light petroleum (b. p. 80—100°) (charcoal) as needles (14·3 g., 89%), m. p. 151°.

To a suspension of the acid chloride (14·2 g.) in acetone (150 ml.) at 0°, sodium azide (5·4 g., 50% excess) in water (13 ml.) was added dropwise with stirring. After being stirred for a further 20 min. the mixture was treated with water (200 ml.) and extracted into benzene (250 ml.). The benzene solution was washed with water (3 × 200 ml.), then dried (Na_2SO_4), and 50 ml. of the benzene were distilled off under reduced pressure. The solution was restored to 250 ml. by the addition of dry benzene and then refluxed gently for 3½ hr., by which time the evolution of nitrogen had ceased. Evaporation of the solution afforded the isocyanate (II; R = CNO), m. p. 78° [from benzene–light petroleum (b. p. 60—80°)].

The isocyanate was refluxed with stirring with concentrated hydrochloric acid (150 ml.) for 1 hr. On cooling, the *amine* (II; R = NH_2) *hydrochloride* separated. It crystallised from

---

[14] Dornfeld and Coleman, *Org. Synth.*, Coll. Vol. III, 1955, p. 701.

[15] Allen, Kibler, McLachlin, and Wilson, *ibid.*, p. 28.

dilute hydrochloric acid as plates (9·8 g., 72%), m. p. 244° (Found: C, 73·7; H, 6·0; N, 5·5; Cl, 14·5. $C_{15}H_{14}NCl$ requires C, 73·9; H, 5·8; N, 5·7; Cl, 14·6%). Liberation of the base gave a white solid which readily became yellow in air.

Diazotisation.—(a) *In dilute acid.* Sodium nitrite (0·7 g., 100% excess) in water (10 ml.) was added dropwise during 30 min. with stirring to the amine hydrochloride (1·5 g.) in 2N-hydrochloric acid (20 ml.) and ether (30 ml.) at −5°. The mixture was stirred for 30 min. at 18°, then warmed at 30—35° for 30 min. The ether layer was washed with 2N-ammonia, then water, and dried (Na_2SO_4). Evaporation of the ether gave a yellow resin.

(b) *In concentrated acid.* The amine hydrochloride (5·0 g.) was dissolved in concentrated hydrochloric acid (140 ml.), acetic acid (20 ml.), and ether (100 ml.). Sodium nitrite (2·5 g., 100% excess) in water (10 ml.) was added dropwise during 45 min. to the stirred mixture at 0°. The mixture was then stirred for 1 hr. at 18°, water (250 ml.) was then added, and the ether layer was separated off. The ethereal solution was washed well with 2N-ammonia, then water, dried (Na_2SO_4), and evaporated to yield red crystals. These were chromatographed in the minimum quantity of benzene on alumina, with 1 : 1 benzene–light petroleum (b. p. 60—80°) as eluant, to give the *chloride* (II; R = Cl) (1·8 g., 40%), needles, m. p. 90·5—91° (from ethanol) (Found: C, 79·6; H, 5·2; Cl, 15·5. $C_{15}H_{11}Cl$ requires C, 79·5; H, 4·9; Cl, 15·6%), $\lambda_{max.}$ (in ethanol) 218—222, 238, 246, 276, 283—287 (infl.), 300, 312 mμ (log ε 4·63, 4·29, 4·27, 4·06, 3·99, 3·62, 3·65 respectively).

We thank the D.S.I.R. for a maintenance grant (to C. R. G.) and the University of London for a grant for spectroscopic equipment.

QUEEN MARY COLLEGE (UNIVERSITY OF LONDON),
MILE END ROAD, LONDON, E.1.

[*Received, March* 25*th*, 1959.