

### 78. *Methylperylene*s. Part II.\* *Synthesis of 2,8- and 3,9-Dimethylperylene*.

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2,8- and 3,9-Dimethylperylene have been prepared by a modification of Postovskii and Bednyagina's synthesis<sup>1</sup> of perylene. The ultraviolet spectra of methyl-substituted perylenes are discussed.

IN order to study further the effect of methyl substitution on the ultraviolet absorption spectrum of perylene we have prepared 2,8- and 3,9-dimethylperylene by a method somewhat similar to Postovskii and Bednyagina's synthesis<sup>1</sup> of perylene. The only dimethylperylene previously described are 2,11-dimethylperylene prepared by Royer,<sup>2</sup> and a dimethylperylene of unknown structure prepared by Buu-Hoi,<sup>3</sup> but their spectral properties are not given.

*2,8-Dimethylperylene*.—Reaction of diethyl methylmalonate with 9,10-di(chloromethyl)anthracene gives the expected tetracarboxylic ester (I; R = Me) although the yield is not good owing to a competing reaction which affords 9,10-di(ethoxymethyl)anthracene. The tetracarboxylic acid obtained on hydrolysis of the ester is smoothly decarboxylated in refluxing diphenyl ether to give 9,10-di-(2-carboxypropyl)anthracene. Although this acid should give a perylene derivative directly on cyclisation it was found that the product of such a cyclisation was rather difficult to purify owing to its insolubility. The acid was reduced to the corresponding 9,10-dihydroanthracene derivative (II; R = Me) by sodium in pentyl alcohol and then cyclised with anhydrous hydrogen fluoride. This gave good yields of the 3,9-dioxoperylene derivative (III; R = Me) if the reduced acid (II; R = Me) was added to the anhydrous hydrogen fluoride, but mainly a black tar if the anhydrous hydrogen fluoride was poured on the reduced acid. Although the cyclisation may proceed in either of two possible directions only one product was obtained in our experiments. This is evidently the perylene derivative (III; R = Me) rather than a derivative of 1,2-benzopyrene since reduction and dehydrogenation give a compound having an ultraviolet absorption spectrum closely resembling that of perylene. This compound is then 2,8-dimethylperylene.

*3,9-Dimethylperylene*.—Synthesis of 3,9-dimethylperylene was accomplished by using a similar reaction series. Hydrolysis and decarboxylation of the tetracarboxylic ester

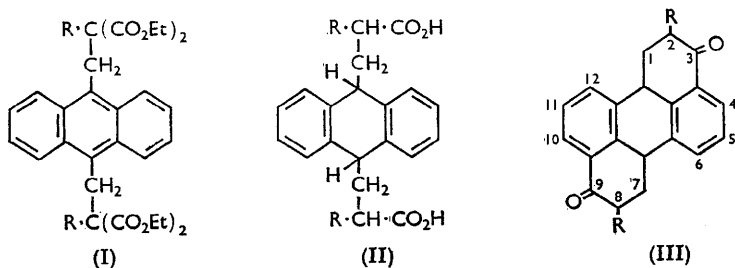
\* Part I, *J.*, 1959, 3526.

<sup>1</sup> Postovskii and Bednyagina, *J. Gen. Chem. (U.S.S.R.)*, 1937, **7**, 2919.

<sup>2</sup> Royer, *Ann. Chim. (France)*, 1946, **1**, 395, 427.

<sup>3</sup> Buu-Hoi, *Rec. Trav. chim.*, 1956, **75**, 1221.

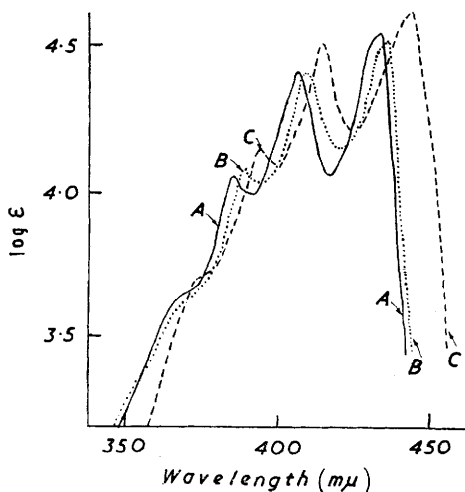
(I; R = H) obtained from diethyl malonate and 9,10-di(chloromethyl)anthracene gave 9,10-di-(2-carboxyethyl)anthracene. Postovskii and Bednyagina<sup>1</sup> described the cyclisation of the chloride of this acid in the presence of anhydrous aluminium chloride, but the insoluble refractory nature of the product made it unsuitable for reaction with a Grignard reagent. We therefore reduced the acid to the dihydroanthracene derivative (II; R = H) and cyclised this in the presence of anhydrous hydrogen fluoride as in the synthesis of



2,8-dimethylperylene. The structure of the resulting 3,9-dioxoperylene derivative (III; R = H) was confirmed by reduction followed by dehydrogenation to perylene. The diketone (III; R = H) with methylmagnesium iodide gave three products. The main product was a tetrahydro-3,9-dimethylperylene which was readily dehydrogenated in the presence of palladium to 3,9-dimethylperylene. The other two products were 3,9-dimethylperylene, apparently formed by disproportionation of the tetrahydro-derivative, and a ketone which was readily reduced and dehydrogenated to 3-methylperylene identical with that described by Buu-Hoi.<sup>3</sup> This ketonic material must arise from condensation of one mol. of Grignard reagent with one of the diketone.

The ultraviolet spectra of perylene, 2,8-dimethylperylene, and 3,9-dimethylperylene in the region 340—450  $m\mu$  are shown in the Figure: the principal peaks are tabulated in the Experimental section.

Absorption spectra for 95% ethanol solutions of (A) perylene and (B) 2,8- and (C) 3,9-dimethylperylene.



*Ultraviolet Absorption Spectra of Methylperylene.*—The small hypsochromic shift in the absorption spectrum (in 95% ethanol) on methylation of perylene at position 1 (reported in Part I) suggested a closer examination of the spectra of methylperylene, since substitution in an alternant hydrocarbon should always cause a bathochromic displacement, whether or not steric hindrance is present.<sup>4,5</sup> In fact, the spectra of perylene and of

<sup>4</sup> Jones, *Chem. Rev.*, 1943, **22**, 1.

<sup>5</sup> Peters, *J.*, 1957, 646.

1-methylperylene in cyclohexane show considerable vibrational fine structure, and confirm the view that substitution causes a small bathochromic displacement (0.5  $m\mu$ ) in the positions of the initial  $p$ -bands.

Since perylene can be regarded as two naphthalene molecules joined by two bonds of low bond order (cf. ref. 6), it is not surprising that the bathochromic shift (6  $m\mu$ ) produced in the  $p$ -bands by methylation at position 3 (see Part I) should be similar to that produced by methylation of naphthalene at position 1 (6  $m\mu$ ).<sup>5</sup> Positions 1 and 2 in perylene are then equivalent to positions 2 and 3 in naphthalene (bathochromic shift on methylation 0  $m\mu$ ).

#### EXPERIMENTAL

9,10-Di-(2,2-bisethoxycarbonylpropyl)anthracene (I; R = Me).—Diethyl methylmalonate (18 g.) was added dropwise with stirring and cooling to a solution made from sodium (2.5 g.) and dry ethanol (200 c.c.). The solution was stirred for a further 15 min., 9,10-di(chloromethyl)-anthracene (15 g.) was added and the mixture was refluxed for 2 hr. When cold the mixture was poured into water, and the solid was filtered off and taken up in ethanol containing a little benzene, from which the ester (14.5 g.) crystallised as pale yellow prisms, m. p. 93° (Found: C, 69.8; H, 6.7.  $C_{32}H_{38}O_8$  requires C, 69.8; H, 6.9%). 9,10-Di(ethoxymethyl)anthracene (9 g.), m. p. 138°, was obtained from the mother-liquor (Found: C, 81.8; H, 7.0. Calc. for  $C_{20}H_{22}O_2$ : C, 81.6; H, 7.5%).

9,10-Di-(2-carboxypropyl)anthracene.—The above ester (8 g.) was hydrolysed for 4 hr. with potassium hydroxide (15 g.) in boiling 50% aqueous ethanol (60 c.c.). The cooled solution was acidified with ~5N-hydrochloric acid, and the precipitate was filtered off and air-dried. This crude acid (4 g.) was decarboxylated by refluxing it in diphenyl ether (35 c.c.) for 1 hr. The solution was cooled to 40°, and ether was added to precipitate the crude product. This material was filtered off, combined with further quantities of the same compound obtained by extracting the ether layer with aqueous sodium hydroxide, and recrystallised from ethanol, to give the acid (3.1 g.), m. p. 278—280° (Found: C, 75.8; H, 6.1.  $C_{22}H_{22}O_4$  requires C, 75.4; H, 6.3%).

9,10-Di-(2-carboxypropyl)-9,10-dihydroanthracene (II; R = Me).—The above acid (3.1 g.) in pentyl alcohol (50 c.c.) was refluxed on an oil-bath at 210° while sodium (10 g.) was added in 2 hr. Further pentyl alcohol (5 × 10 c.c.) was added from time to time. After 3 hours' refluxing, the cooled mixture was poured into water and steam-distilled to remove the alcohol. The solution was clarified with charcoal, filtered, and acidified to afford the acid (3 g.). A sample, recrystallised from ethanol, had m. p. 258° (Found: C, 74.9; H, 7.0.  $C_{22}H_{24}O_4$  requires C, 75.0; H, 6.9%).

1,2,3,6b,7,8,9,12b-Octahydro-2,8-dimethyl-3,9-dioxoperylene (III; R = Me).—The crude acid (II; R = Me) (3 g.) was added as a powder to anhydrous hydrogen fluoride (100 c.c.). After 18 hr. at room temperature the mixture was poured on ice, and the precipitate was filtered off, washed with aqueous sodium hydroxide, and taken up in ethyl acetate from which yellow crystals (1.5 g.) were deposited. These crystals, which redissolved in ethyl acetate with difficulty, were recrystallised from benzene, to give the dioxoperylene derivative, m. p. 238—240° (decomp.) (Found: C, 83.6; H, 6.3.  $C_{32}H_{20}O_2$  requires C, 83.5; H, 6.4%).

2,8-Dimethylperylene.—The above diketone (0.3 g.) was extracted from a thimble with refluxing ether into lithium aluminium hydride (0.3 g.) in dry ether (200 c.c.) during 8 hr. Ethyl acetate was added to destroy the excess of reagent, the mixture was poured on ice and sulphuric acid, and the ether layer was separated and evaporated to dryness. The resulting white solid was refluxed for 7 hr. in 2-methylnaphthalene (25 c.c.) containing 5% palladium-charcoal (0.2 g.). Most of the solvent was distilled off and the residue was taken up in hexane (50 c.c.) and chromatographed on alumina. Elution with hexane removed the 2-methylnaphthalene. The yellow band of 2,8-dimethylperylene was eluted with benzene-hexane from which it crystallised on concentration as yellow needles (0.23 g.), m. p. 249—250° (Found: C, 94.5; H, 5.55.  $C_{22}H_{16}$  requires C, 94.25; H, 5.75%). It gave a picrate, as black needles, m. p. 228—230° (from benzene) (Found: N, 7.8.  $C_{28}H_{19}O_7N_3$  requires N, 8.2%), and a derivative with trinitrobenzene as black needles, m. p. 247—248° (Found: N, 8.2.  $C_{28}H_{19}O_6N_3$  requires N, 8.5%).

9,10-Di-(2-carboxyethyl)-9,10-dihydroanthracene (II; R = H).—9,10-Di-(2-carboxyethyl)-anthracene (6.3 g.), m. p. 254—255°, in pentyl alcohol (150 c.c.) was heated to reflux in an oil-bath while sodium (20 g.) was added in portions during 5 hr. The solution became clear in

<sup>5</sup> Donaldson, Robertson, and White, *Proc. Roy. Soc.*, 1953, A, 220, 311.

3 hr. and further pentyl alcohol ( $4 \times 25$  c.c.) was added when the mixture started to solidify. The mixture was poured into water, steam-distilled to remove the pentyl alcohol, clarified with charcoal, and acidified. The solid was filtered off and recrystallised from ethanol to give the *dihydroanthracene* derivative as white plates, m. p. 250—251° (4.5 g.) (Found: C, 74.3; H, 6.3.  $C_{20}H_{20}O_4$  requires C, 74.1; H, 6.2%).

1,2,3,6b,7,8,9,12b-Octahydro-3,9-dioxoperylene (III; R = H).—The acid (II; R = H) (4.0 g.) was added to anhydrous hydrogen fluoride (100 c.c.) at room temperature and set aside for 16 hr. The mixture was poured on ice, and the solid filtered off and taken up in ethyl acetate. After being washed with dilute aqueous potassium hydroxide the extract was dried and concentrated, to give the *diketone* as almost colourless needles (3.1 g.) which quickly darkened to a pale golden colour and had m. p. 239—240° (decomp.) (Found: C, 83.1; H, 5.9.  $C_{20}H_{16}O_2$  requires C, 83.3; H, 5.6%). A sample was reduced with excess of lithium aluminium hydride in ether, and the product, without purification, was dehydrogenated and dehydrated by refluxing it with 5% palladium-charcoal in 2-methylnaphthalene, to give perylene, m. p. 272—273° after purification by chromatography on alumina.

1,6b,7,12b-Tetrahydro-3,9-dimethylperylene.—The diketone (III; R = H) (2.0 g.) was extracted with refluxing benzene during 2 hr. from a thimble into a Grignard reagent prepared from methyl iodide (5.0 g.) and magnesium (0.7 g.) in ether which was later displaced by benzene (200 c.c.). After a further hour at the b. p. the cooled solution was poured into dilute sulphuric acid, and the benzene was removed by steam-distillation. The yellow residue was filtered off and recrystallised from ethyl acetate, to give the *tetrahydrodimethylperylene* (1.6 g.) as yellow needles, m. p. 207—208° (Found: C, 92.6; H, 6.9.  $C_{22}H_{20}$  requires C, 92.9; H, 7.1%). The residue from the crystallisation was chromatographed on an alumina column in benzene to give 3,9-dimethylperylene (0.1 g.) (see below), followed by ketonic material. The last substance, which was not obtained pure, was reduced with lithium aluminium hydride and dehydrated and dehydrogenated with 5% palladium-charcoal in 2-methylnaphthalene to give, after chromatography in hexane-benzene on an alumina column, golden plates of 3-methylperylene, m. p. 214—215° (Found: C, 94.5; H, 5.2. Calc. for  $C_{21}H_{14}$ : C, 94.7; H, 5.3%).

3,9-Dimethylperylene.—The preceding tetrahydroperylene (0.9 g.) in 2-methylnaphthalene (5.0 g.) was refluxed for 3 hr. with 5% palladium-charcoal (0.1 g.). The cooled mixture was chromatographed in 1 : 1 benzene-hexane on alumina, to give the *dimethylperylene* as yellow plates, m. p. 249—250° (Found: C, 94.5; H, 5.6.  $C_{22}H_{16}$  requires C, 94.3; H, 5.7%). It gave a *picrate* from benzene as black needles, m. p. 224° after decomp. (Found: C, 66.2; H, 3.7.  $C_{28}H_{18}O_7N_3$  requires C, 66.0; H, 3.8%), and a *trinitrobenzene derivative* as black needles (from benzene-ethanol), m. p. 259—260° (Found: C, 68.5; H, 3.6.  $C_{28}H_{18}O_6N_3$  requires C, 68.15; H, 3.9%).

*Absorption Spectra*.—Quantitative ultraviolet absorption spectra (see Table below) were obtained on a Beckman model DK2 spectrophotometer by courtesy of the Nutrition Research Department, Otago Medical School.

*Absorption spectra (m $\mu$  and log  $\epsilon$ ) in 95% ethanol.*

Perylene .....	208	245	252	266 (infl.)	364 (infl.)	385	406.5	434
	4.73	4.52	4.66	3.93	3.60	4.05	4.40	4.54
2,8-Dimethylperylene	209	247	254	270 (infl.)	372 (infl.)	389	410	436
	4.73	4.52	4.67	4.00	3.62	4.07	4.41	4.51
3,9-Dimethylperylene	210	248	255.4	268 (infl.)	375 (infl.)	394	415	444
	4.74	4.52	4.65	4.00	3.70	4.14	4.50	4.61

In cyclohexane at 18°. The most distinct bands are:

Perylene: 245.5, 253, 264, —, 352, 369, 387.5, 390.5, 408, 411.5(infl.), 421.5(infl.), 430, 436, 439(infl.) m $\mu$ .

1-Methylperylene: 245, 253, 265, 292, 350(infl.), 367.5, 386.5, 390, 408.5, 412(infl.), 422, 430.5, 436.5, 440(infl.) m $\mu$ .

3,9-Dimethylperylene: 249, 257, 268(infl.), 295, 418, 442.4(infl.), 448 m $\mu$ .

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