709. *Methylperylenes. Part I. Synthesis of* 1-, 2-, *and* 3-*Methylperylene.*

By A. D. Campbell, R. A. Elder, and G. W. Emerson.

The three monomethylperylenes have been synthesised and their ultraviolet spectra determined. 1-Methylperylene was prepared by the cyclodehydrogenation of a methyl-1,1′-binaphthyl; 2-methylperylene from 2-methylanthracene by a variation of a Postovskii and Bednyagina [1] perylene synthesis; and 3-methylperylene by a modification of Buu-Hoï's method [2] from 3-formylperylene.

During a recent investigation [3] on the structure of a fungus pigment, degradative work yielded small amounts of a hydrocarbon, the ultraviolet absorption spectrum of which agreed closely with that reported for perylene. Since insufficient material was available for analysis the possibility of the hydrocarbon's being an alkylperylene could not be overlooked, particularly since only one perylene homologue was then known and its spectrum had not been recorded. Plausible biogenetic schemes would allow the pigment to be related to 2,8- or 2,11-dimethylperylene, and initially the synthesis of the former was undertaken. It seemed of interest to examine further the effect of alkyl-substitution on the physical properties of perylene, and a number of methyl- and dimethyl-perylenes have been synthesised for this purpose.

1-*Methylperylene.*—Some difficulty was experienced in synthesising this compound but success was finally attained by using a methylbinaphthyl as intermediate. Condensation of the lithium derivative from 1-bromo-2-methylnaphthalene with α-tetralone gave a poor yield of 3,4-dihydro-2′-methyl-1,1′-binaphthyl (I) as a glass, and dehydrogenation of this with palladium on charcoal led to 2-methyl-1,1′-binaphthyl and 1-methylperylene (II). The latter hydrocarbon gave two derivatives with picric acid, a black monopicrate under controlled conditions, and a brick-red dipicrate in the presence of excess of picric acid.

Other methods were unsuccessful. Chloromethylation of 1-methylanthracene was unsatisfactory, preventing the use of the Postovskii and Bednyagina perylene synthesis as adapted to the preparation of 2-methylperylene below. In another investigation no perylene derivative was isolated on dehydrogenation of the product obtained from crotonaldehyde and tetrahydrobenzanthrone in hydrogen fluoride, although Calcott *et al.*[4] obtained perylene by this method, condensing acraldehyde with tetrahydrobenzanthrone.

2- *and* 3-*Methylperylene.*—2-Methylperylene was obtained by making use of a series of

---

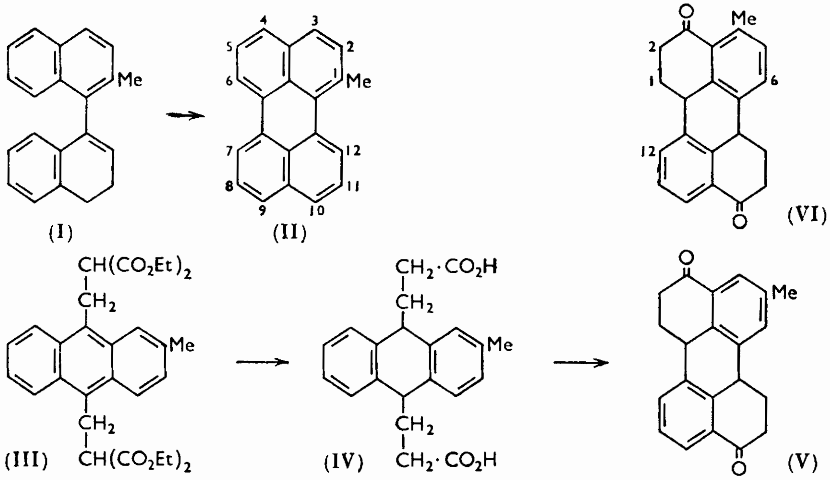
[1] Postovskii and Bednyagina, *J. Gen. Chem.* (*U.S.S.R.*), 1937, **7**, 2919.

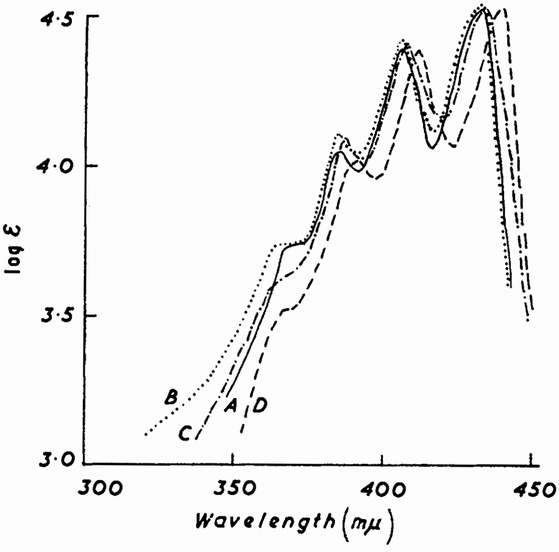
[2] Buu-Hoï, *Rec. Trav. chim.*, 1956, **75**, 1221.

[3] Anderson and Murray, *Chem. and Ind.*, 1956, 376.

[4] Calcott, Tinker, and Weinmayer, *J. Amer. Chem. Soc.*, 1939, **61**, 949.

reactions similar to the Postovskii and Bednyagina[1] synthesis of perylene. The 9,10-bischloromethyl derivative of 2-methylanthracene with diethyl malonate gave a tetracarboxylic ester (III) which on hydrolysis and decarboxylation gave 9,10-di-(2-carboxyethyl)-2-methylanthracene. This acid was not cyclised directly but was reduced to the dihydroanthracene derivative (IV), which was smoothly cyclised by anhydrous hydrogen fluoride to a mixture of the two possible dioxoperylenes. The minor constituent of this mixture, on reduction and dehydrogenation, gave 3-methylperylene identical with that prepared from perylene by Buu-Hoï.[2] It must therefore be 1,2,3,6b,7,8,9,12b-octahydro-4-methyl-3,9-dioxoperylene (VI). The other isomer (V) afforded 2-methylperylene when similarly reduced and dehydrogenated. Although it would also be possible to obtain a derivative of 1,2-benzopyrene in this cyclisation there was no evidence for the presence of such a compound.





Ultraviolet absorption spectra of (A) perylene and (B) 1-, (C) 2-, and (D) 3-methylperylene in 95% ethanol.

Buu-Hoï [2] describes a synthesis of 3-methylperylene *via* 3-formylperylene but gives no ultraviolet spectrum. We have repeated the formylation of perylene and have simplified the reduction of this substance to 3-methylperylene.

Spectra.—The principal peaks in the ultraviolet absorption spectra of perylene and its three monomethyl derivatives are tabulated on p. 3529 and the spectra in the region 340—450 mμ are shown in the Figure.

EXPERIMENTAL

3,4-*Dihydro*-2′-*methyl*-1,1′-*binaphthyl* (I).—Lithium (2·8 g.) in thin slices was added to a solution of 1-bromo-2-methylnaphthalene (44 g.) in dry ether (300 c.c.). The mixture was stirred at reflux for 3 hr., most of the lithium dissolving. α-Tetralone (29 g.) in ether (100 c.c.) was then added during 45 min. and the resulting solution was refluxed for a further 2 hr. It was poured into ice-cold sulphuric acid, and the ether layer was dried and distilled, to give a mixture of unchanged starting materials, followed by the *dihydro-binaphthyl* (I) (5 g.), b. p. 250—260°/20 mm. (Found: C, 92·9; H, 6·6. $C_{21}H_{18}$ requires C, 93·3; H, 6·7%).

1-*Methylperylene* (II).—The above dihydrobinaphthyl (3 g.) was refluxed (bath 340—350°) for 3 hr. with 5% palladium–charcoal (1 g.) in a stream of carbon dioxide. The cooled mass was taken up in the minimum quantity of hexane containing a trace of benzene and chromatographed on an alumina column. Elution with hexane gave a colourless band which showed a blue fluorescence under ultraviolet radiation. Concentration of this fraction gave 2-*methyl*-1,1′-*binaphthyl* (2 g.) which, after recrystallisation from hexane, had m. p. 120—122° (Found: C, 94·0; H, 5·8. $C_{21}H_{16}$ requires C, 94·0; H, 6·0%). The remaining yellow band was eluted with benzene–hexane which deposited yellow crystals on concentration. This material was filtered off and converted into a picrate which was subsequently decomposed in benzene on alumina. Yellow plates of 1-*methylperylene* (30 mg.), m. p. 258—260° with sintering at 220°, were obtained by crystallisation from benzene–hexane (Found: C, 94·7; H, 5·0. $C_{21}H_{14}$ requires C, 94·7; H, 5·3%). It gave a *monopicrate* as black needles (from benzene–hexane), m. p. 191—192° (Found: C, 65·3; H, 3·0; N, 8·3. $C_{27}H_{17}O_7N_3$ requires C, 65·45; H, 3·5; N, 8·5%), a *dipicrate* as brick-red needles (from benzene), m. p. 186—187° (Found: C, 54·0; H, 2·7. $C_{33}H_{20}O_{14}N_6$ requires C, 54·6; H, 2·8%), and the *derivative* with trinitrobenzene as dark purple needles, m. p. 242—243° (from benzene–hexane) (Found: C, 67·3; H, 3·5. $C_{27}H_{17}O_6N_3$ requires C, 67·6; H, 3·5%).

9,10-*Bischloromethyl*-2-*methylanthracene*.—2-Methylanthracene (16·5 g.) and paraformaldehyde (15 g.) were added to a mixture of dioxan (150 c.c.) and concentrated hydrochloric acid (25 c.c.) which had been previously saturated with dry hydrogen chloride. The whole was boiled for 2 hr. while dry hydrogen chloride was added, and for a further 3 hr., then cooled and set aside for 12 hr. The crystals (17 g.) which separated recrystallised from dioxan, giving the *bischloromethyl derivative* as yellow needles, m. p. 229—231° (decomp.) (Found: C, 70·7; H, 5·0. $C_{17}H_{14}Cl_2$ requires C, 70·6; H, 4·8%).

9,10-*Bis*-(2,2-*diethoxycarbonylethyl*)-2-*methylanthracene* (III).—Diethyl malonate (18·2 g.) was added dropwise with stirring to a solution made by adding sodium (2·6 g.) to pure dry ethanol (200 c.c.), and the mixture was stirred at the b. p. for a further 30 min. The above bischloromethyl compound (14 g.) was then added all at once, and the mixture was refluxed with stirring for 2 hr. and poured into cold water slightly acidified with acetic acid. The precipitate was filtered off to give the *tetra-ethyl ester* (III) (21 g.) as pale yellow needles, m. p. 140—141° (from ethanol) (Found: C, 69·8; H, 6·7. $C_{31}H_{36}O_8$ requires C, 69·4; H, 6·8%).

9,10-*Di*-(2-*carboxyethyl*)-2-*methylanthracene*.—The above ester (23 g.) was refluxed for 4 hr. with potassium hydroxide (50 g.) in 50% aqueous ethanol (200 c.c.). The cooled solution was filtered and the filtrate was acidified with dilute hydrochloric acid. The resulting precipitate was filtered off, air-dried (yield, 12 g.), and then refluxed in diphenyl ether (50 c.c.) for 1 hr. Ether (100 c.c.) was added to the cooled solution, and the acid which crystallised (3 g.) was filtered off. Further acid (4 g.) was obtained by extracting the filtrate with aqueous sodium hydroxide. Recrystallisation of the combined acids from benzene containing a trace of ethanol gave the *dipropionic acid* (5·8 g.) as pale yellow needles, m. p. 215—216° (Found: C, 75·0; H, 6·0. $C_{21}H_{20}O_4$ requires C, 75·0; H, 6·0%).

9,10-*Di*-(2-*carboxyethyl*)-9,10-*dihydro*-2-*methylanthracene* (IV).—Sodium (20 g.) was added in small portions during 12 hr. to the above dipropionic acid (5·8 g.) in boiling pentyl alcohol (150 c.c.). The mixture was cautiously poured into water and the pentyl alcohol was removed by steam-distillation. The aqueous solution was filtered, then acidified with dilute hydrochloric acid, and the resulting white solid was filtered off. Recrystallisation from ethanol gave the *dihydro-compound* (4·0 g.) as white plates, m. p. 228° (Found: C, 74·2; H, 6·1. $C_{21}H_{22}O_4$ requires C, 74·5; H, 6·55%).

Cyclisation of 9,10-*Di*-(2-*carboxyethyl*)-9,10-*dihydro*-2-*methylanthracene*.—The above dihydroanthracene derivative (0·6 g.) was treated with anhydrous hydrogen fluoride (30 c.c.) at room temperature. After 24 hr. the resulting solution was poured on ice, and the solid material was filtered off, taken up in ethyl acetate, and washed with aqueous sodium carbonate. Neutral cyclised material (0·2 g.) which separated on concentration of the ethyl acetate solution was further recrystallised from ethyl acetate, to give 1,2,3,6*b*,7,8,9,12*b*-*octahydro*-5-*methyl*-3,9-*dioxoperylene* (V) (0·18 g.) as pale green needles, m. p. 215—217° (decomp.) (Found: C, 83·2; H, 6·0. $C_{21}H_{18}O_2$ requires C, 83·4; H, 6·0%). The mother-liquors from the above crystallisations, on concentration, gave red crystals which on further recrystallisation from ethyl acetate (charcoal) gave 1,2,3,6*b*,7,8,9,12*b*-*octahydro*-4-*methyl*-3,9-*dioxoperylene* (VI) (0·05 g.) as brick-red crystals, m. p. 193—194° (Found: C, 83·6; H, 5·8. $C_{21}H_{18}O_4$ requires C, 83·4; H, 6·0%). The latter compound gave 3-methylperylene, m. p. 214—215°, on reduction with lithium aluminium hydride followed by dehydration and dehydrogenation in refluxing 2-methylnaphthalene in the presence of palladium–charcoal.

2-*Methylperylene*.—1,2,3,6b,7,8,9,12b-Octahydro-5-methyl-3,9-dioxoperylene (V) (0·15 g.) was extracted with refluxing ether into excess of lithium aluminium hydride (0·3 g.) in dry ether (200 c.c.) during 8 hr. Excess of reagent was decomposed by ethyl acetate, the resulting solution was poured into ice and dilute sulphuric acid, the ether layer was separated, and the aqueous solution extracted with ether. The residue obtained on evaporation of the combined ether extracts was refluxed in 2-methylnaphthalene (20 g.) in the presence of 5% palladium–charcoal (0·1 g.) for 8 hr. Hexane (100 c.c.) was added to the cooled mixture, and the resulting solution was applied to a column of alumina. 2-Methylnaphthalene was eluted with hexane, and the residual yellow band with benzene–hexane mixtures, to give 2-*methylperylene* (0·07 g.) as yellow prisms, m. p. 168° (from ethanol) (Found: C, 94·65; H, 5·4. $C_{21}H_{14}$ requires C, 94·7; H, 5·3%). It gave a *picrate* as dark brown needles, m. p. 199—200° (decomp.) (from benzene–hexane) (Found: C, 65·45; H, 3·2; N, 8·5. $C_{27}H_{17}O_7N_3$ requires C, 65·5; H, 3·5; N, 8·5%), and a *derivative* with trinitrobenzene as red needles, m. p. 227—228° (decomp. at 220°) (from benzene–ethanol) (Found: C, 67·8; H, 3·1. $C_{27}H_{17}O_6N_3$ requires C, 67·6; H, 3·5%).

3-*Methylperylene*.—3-Formylperylene (0·25 g.) and 85% hydrazine hydrate (0·5 c.c.) were heated in a sealed tube for 5 hr. at 300°. The resulting red solid in benzene was purified on an alumina column, and the eluate was concentrated, to give the hydrocarbon (0·18 g.) as golden plates, m. p. 214° (Buu-Hoï gave m. p. 217°) (Found: C, 94·6; H, 5·2. Calc. for $C_{21}H_{14}$: C, 94·7; H, 5·3%). It gave a picrate as black needles, m. p. 220° with previous softening (Buu-Hoï gives m. p. 226° with decomp. below 212°) (Found: C, 65·5; H, 3·2. Calc. for $C_{27}H_{17}O_7N_3$: C, 65·45; H, 3·5%), and a trinitrobenzene *derivative* as long dark purple needles, m. p. 242° (from benzene–ethanol) (Found: C, 67·8; H, 3·3. $C_{27}H_{17}O_6N_3$ requires C, 67·6; H, 3·5%).

Absorption Spectra.—Ultraviolet absorption spectra were obtained on a Beckman Model DK2 Spectrophotometer by courtesy of the Nutrition Research Department, Otago Medical School, as tabulated.

Absorption spectra (mμ *and* log ε) 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
1-Methylperylene	208	245	252	268 (infl.)	367 (infl.)	384	406	433·5
	4·72	4·52	4·65	3·88	3·70	4·10	4·40	4·52
2-Methylperylene	208	246·5	253	266 (infl.)	370 (infl.)	387	408	435
	4·76	4·51	4·65	3·97	3·90	4·08	4·41	4·53
3-Methylperylene ...	—	246·5	254	268 (infl.)	370 (infl.)	391	412·5	440
	—	4·46	4·61	3·85	3·53	4·02	4·39	4·53

This work has been assisted by grants from the Research Fund of the University of New Zealand and from the Mellor Research Fund. Microanalyses were carried out by the Microanalytical Laboratory of this Department.

CHEMISTRY DEPARTMENT, UNIVERSITY OF OTAGO,
NEW ZEALAND.

[*Received, April* 13*th*, 1959.]