927. *Syntheses of Coronene and* 1 : 2-7 : 8-*Dibenzocoronene.*

By E. Clar and M. Zander.

1 : 12-Benzoperylene-1′ : 2′-dicarboxylic anhydride (II) was obtained in quantitative yield from perylene, maleic anhydride, and chloranil. Decarboxylation gave the hydrocarbon (III) which was condensed to afford coronene-1 : 2-dicarboxylic anhydride (IV) in the same way. Decarboxylation gave coronene in good yield. The tribenzoperylene (VI), condensed with bromomaleic anhydride, afforded the anhydride (VII) which gave 1 : 2-7 : 8-dibenzocoronene on decarboxylation.

The condensation of perylene (I) with maleic anhydride in boiling nitrobenzene as an oxidising agent was described by Clar.[1] We have now obtained quantitative yields of the anhydride (II) by using an excess of boiling maleic anhydride as solvent and chloranil as oxidising agent. Conversion of this anhydride into the hydrocarbon (III) by copper powder in quinoline is very slow, requiring several days: better results were obtained by sublimation with soda-lime in a vacuum.

Fig. 1.

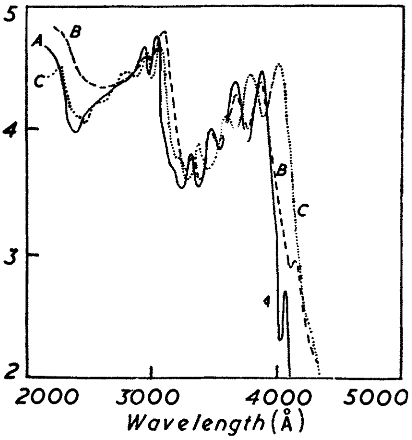

Fig. 2.

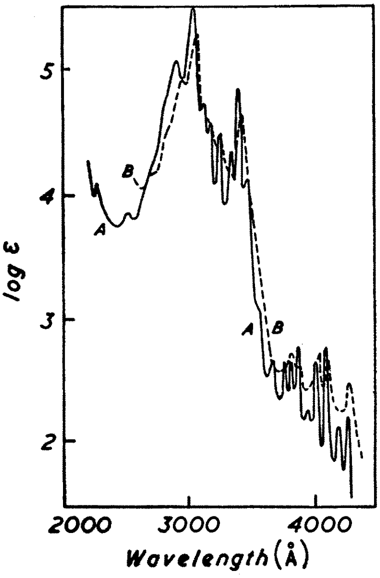

Fig. 1. *Absorption max.* (Å) *and log* ε (*in parentheses*): (*A*) 1 : 12-*benzoperylene* (III) *in* C_6H_6, 4065 (2·75), 3875 (4·45), 3670 (4·40), 3480 (4·02), 3310 (3·80); in EtOH, 3030 (4·75), 2920 (4·65); (*B*) *dipotassium* 1 : 12-*benzoperylene*-1′ : 2′-*dicarboxylate* (*cf.* II) *in* 50% EtOH, 4140 (2·96), 3860 (4·30), 3480 (3·96), 3320 (3·82), 3080 (4·78), 2970 (2·68); (*C*) *dibromo*-1 : 12-*benzoperylene in dioxan*, 4010 (4·54), 3780 (4·46), 3590 (4·13), 3375 (3·91), 3070 (4·73), 2940 (4·62), 2820 (2·48), 2260 (4·52).

Fig. 2. *Absorption max.* (Å) *and log* ε (*in parentheses*): (*A*) *coronene* (V) *in* C_6H_6, 4280 (2·15), 4200 (2·12), 4100 (2·75), 4020 (2·65), 3965 (2·23), 3880 (2·75), 3815 (2·67), 3780 (2·63), 3685 (2·67), 3475 (4·15), 3415 (4·85), 3360 (4·35), 3255 (4·45), 3195 (4·60), 3165 (4·70), 3050 (5·50); *in* EtOH, 2900 (5·10), 2520 (3·88), 2280 (4·08); (*B*) *dipotassium coronene*-1 : 2-*dicarboxylate* (*cf.* IV) *in* 50% EtOH, 4300 (2·47), 4120 (2·63), 4060 (2·71), 3900 (2·61), 3830 (2·70), 3430 (4·67), 3280 (4·41), 3070 (5·027), 2950 (4·89).

It has been reported that 1 : 12-benzoperylene (III) could not be further condensed with maleic anhydride in boiling nitrobenzene.[1] However, this condensation to coronene-1 : 2-dicarboxylic anhydride (IV) was easily achieved by the modification just mentioned, and coronene was easily obtained by decarboxylation. The overall yield being 25% from

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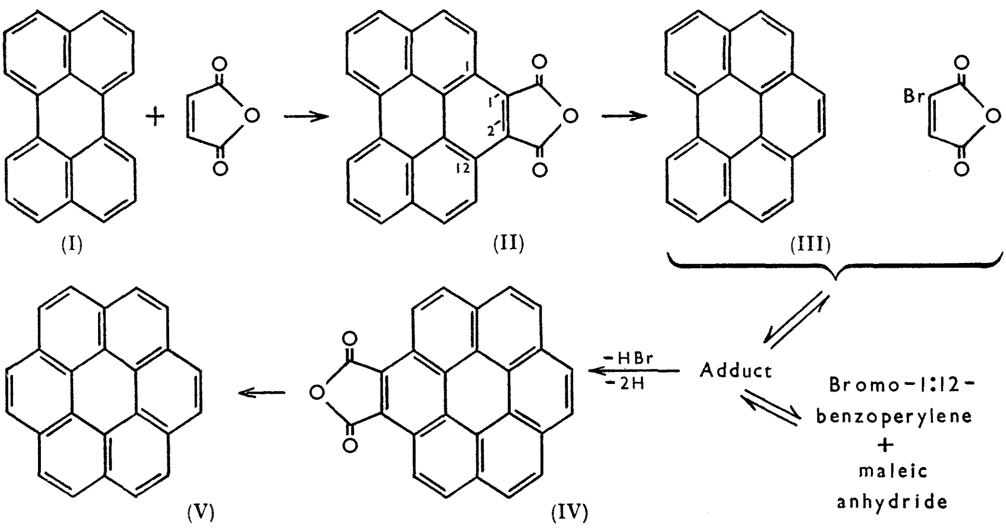
[1] Clar, *Ber.*, 1932, **65**, 846.

commercial perylene and 41% from 1 : 12-benzoperylene, this is the simplest and most efficient synthesis of coronene.

The above results can be best explained by assumption of a dissociable adduct of



perylene or 1 : 12-benzoperylene and maleic anhydride which precedes the dehydrogenation to the aromatic anhydrides (II) or (IV). This is supported by the application of bromomaleic anhydride, instead of maleic anhydride, in the case of 1 : 12-benzoperylene.

FIG. 3.

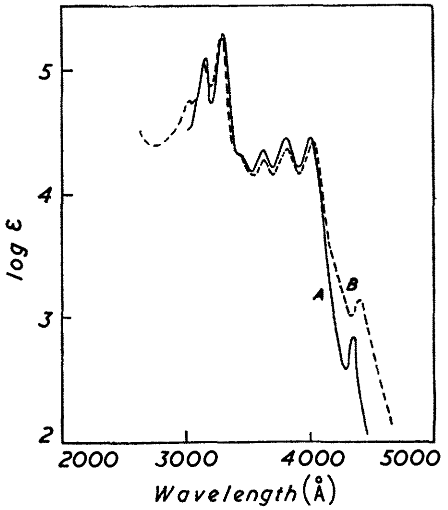


FIG. 4.

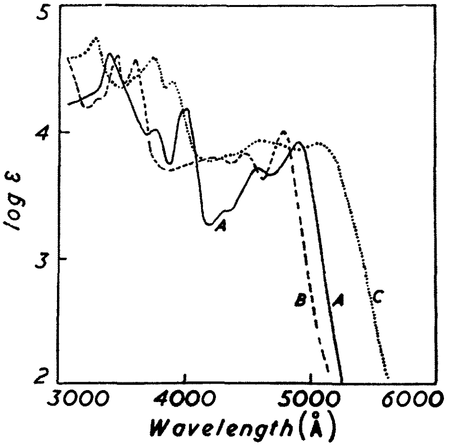
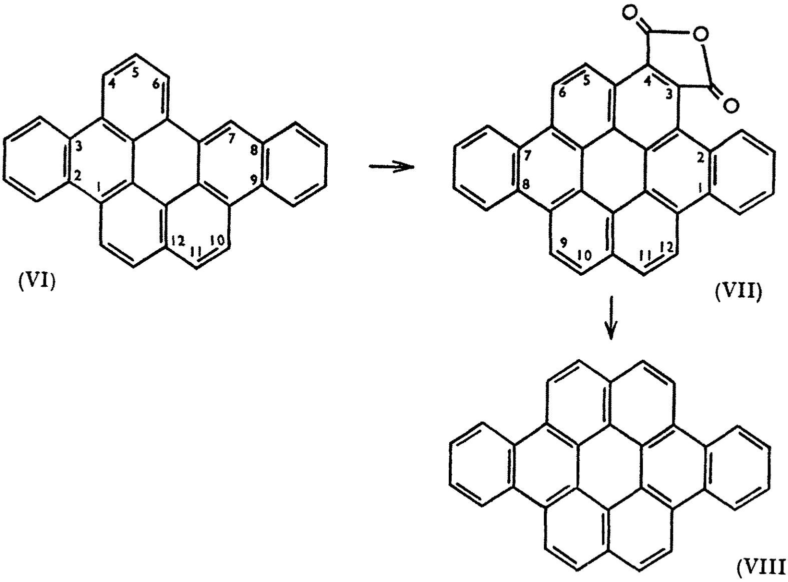


FIG. 3. *Absorption max.* (Å) *and log* ε (*in parentheses*): (*A*) 1 : 2-7 : 8-*dibenzocoronene* (VIII) *in* $C_6H_3Cl_3$, 4350 (2·84), 4010 (4·46), 3810 (4·44), 3630 (4·32), 3300 (5·29), 3160 (5·07); (*B*) *dipotassium* 1 : 2-7 : 8-*dibenzocoronene*-5 : 6-*dicarboxylate* (*cf.* VII) *in* 50% EtOH, 4380 (3·17), 4020 (4·42), 3820 (4·38), 3635 (4·28), 3280 (5·30), 3150 (5·01), 3030 (4·73).

FIG. 4. *Absorption max.* (Å) *and log* ε (*in parentheses*): (*A*) 1 : 12-*benzoperylene*-1' : 2'-*dicarboxylic anhydride* (II) *in* $C_6H_3Cl_3$, 4880 (3·88), 4575 (3·72), 4000 (4·18), 3775 (4·02), 3400 (4·62); (*B*) *coronene*-1 : 2-*dicarboxylic anhydride* (IV) *in* $C_6H_3Cl_3$, 4780 (3·99), 4470 (3·82), 4230 (3·81), 3620 (4·58), 3460 (4·59), 3080 (4·54); (*C*) 1 : 2-7 : 8-*dibenzocoronene*-5 : 6-*dicarboxylic anhydride* (VII) *in* $C_6H_3Cl_3$, 5050 (3·91), 4610 (3·93), 3900 (4·41), 3750 (4·59), 3290 (3·73).

The dissociation of this adduct could lead to bromobenzoperylene and maleic anhydride. In fact, this reaction gave only 20% (% of product) of alkali-soluble and 80% of alkali-insoluble product. The latter consisted mainly of a uniform crystalline dibromo-1 : 12-benzoperylene, which could have been formed only by the repetition of the assumed addition and dissociation with the initial product, bromo-1 : 12-benzoperylene and bromomaleic anhydride. The formation of bromobenzoperylenes involves migration of bromine in the dissociable adduct.

In this reaction bromomaleic anhydride acts also as an oxidising agent. When this part in the condensation was taken over by chloranil the yield of coronenedicarboxylic anhydride (IV) rose to 43%. However, this anhydride contained 3·5% of bromine, though reaction with soda-lime and copper powder still gave pure coronene. The formation of a bromine-containing anhydride (IV) indicates that bromo-1 : 12-benzoperylene can also participate in the condensation.



(VI)

(VII)

(VIII)

The tribenzoperylene [2] (VI), which proved to be more reactive than benzoperylene (III), condensed smoothly with bromomaleic anhydride to give the anhydride (VII), with no indication of bromination. Excellent yields were also obtained by using maleic anhydride and chloranil. 1 : 2-7 : 8-Dibenzocoronene (VIII) was then obtained in good yield.

The absorption spectra agree with the presumed structures. 1 : 12-Benzoperylene (III), its dibromo-derivative, and its dicarboxylic acid have very similar spectra (Fig. 1). The same is the case with coronene (V) and its dicarboxylic acid (Fig. 2), and with 1 : 2-7 : 8-dibenzocoronene (VIII) and its dicarboxylic acid (Fig. 3). No endocyclic addition of maleic anhydride could account for such a close relationship. The anhydrides (II), (IV), and (VII) show absorption at similar wavelengths in the visible spectra, whilst considerable differences were recorded in the ultraviolet: this might suggest that the visible bands are associated with the anhydride ring.

EXPERIMENTAL

M.p.s were taken in evacuated capillaries. Microanalyses are by Mr. J. M. Cameron and Miss M. W. Christie.

1 : *12-Benzoperylene-*1′ : *2′-dicarboxylic anhydride* (II).—Commercial perylene (Shore Transit Company Ltd., 80 Wolmer Gardens, Edgware, Middlesex) (10 g.) was dissolved in boiling maleic anhydride (150 g.), and chloranil (21 g.) added in portions. The red brown anhydride crystallised almost immediately. After 10 minutes' refluxing, hot xylene (200 ml.) was added, the

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[2] Clar, *Chem. Ber.*, 1949, **82**, 53.

warm mixture was filtered, and the red brown needles (12·8 g.) were washed with xylene and ether.

1 : 12-*Benzoperylene* (III).—Benzoperylenedicarboxylic anhydride (5·5 g.) and soda-lime (16·5 g.) were powdered together and heated at 350° for 1 hr. The sublimation-apparatus was evacuated (0·02 mm.) and the temperature raised to 440° for 9½ hr. The sublimate (2·7 g.) recrystallised from xylene in large plates, m. p. 273°.[1] With copper powder in boiling quinoline only 10% of the anhydride was decarboxylated in 2 days.

Coronene-1 : 2-*dicarboxylic Anhydride* (IV).—(*a*) 1 : 12-Benzoperylene (2 g.) and chloranil (7·2 g.) in maleic anhydride (20 g.) were refluxed for 5 hr. Hydrogen chloride was evolved and dark red needles crystallised from the hot mixture. Warm nitrobenzene (30 ml.) was added, the suspension was cooled to about 70°, and the needles (2 g.) were filtered off, washed with nitrobenzene and ether, and further purified by extraction with boiling nitrobenzene (50 ml.) (1·7 g.), vacuum-sublimation, and crystallisation from nitrobenzene. The orange-red needles of *anhydride* began to sinter at 455° and melted at 490—503° with decomposition. Hot concentrated sulphuric acid dissolved them with a yellow colour (Found: C, 84·2; H, 2·5. $C_{26}H_{10}O_3$ requires C, 84·3; H, 2·7%).

(*b*) 1 : 12-Benzoperylene (0·5 g.), chloranil (0·44 g.), and bromomaleic anhydride (8 ml.) were refluxed for 75 min. The anhydride (IV) crystallised in needles (0·29 g.) which were filtered off and washed with benzene and ether. After two recrystallisations from nitrobenzene the anhydride still contained 3·5% of bromine. However, it gave pure coronene when sublimed with soda-lime and copper powder.

Dibromo-1 : 12-*benzoperylene.*—1 : 12-Benzoperylene (10 g.) and bromomaleic anhydride (70 ml.) were refluxed for 1 hr. After cooling, xylene (50 ml.) was added and the precipitate filtered off and washed with benzene and ether. Extraction with dilute hot sodium hydroxide solution gave impure coronenedicarboxylic acid (2 g.). The residue (8 g.) was repeatedly extracted with boiling xylene, and the extract treated with charcoal, filtered, and concentrated. *Dibromo*-1 : 12-*benzoperylene* separated in yellow needles. These were chromatographed in benzene on activated alumina. They then melted at 260—262° and dissolved in hot concentrated sulphuric acid to a red-violet solution (Found: C, 60·8; H, 2·6; Br, 36·8. $C_{22}H_{10}Br_2$ requires C, 60·9; H, 2·3; Br, 36·8%).

Coronene (V).—Coronene-1 : 2-dicarboxylic anhydride (0·3 g.) and soda-lime (1 g.) were ground together and heated under nitrogen to 400° for 45 min. The sublimation-apparatus was evacuated and the temperature raised to 420° for 2 hr. Coronene sublimed in pale yellow needles (0·16 g.). Recrystallised from xylene it had m. p. and mixed m. p. 425—428°. Hot sulphuric acid dissolved it with a yellowish-green colour. Decarboxylation could also be effected by prolonged boiling with quinoline and copper powder (Found: C, 96·1; H, 4·2; Calc. for $C_{24}H_{12}$: C, 96·0; H, 4·0%).

1 : 2-7 : 8-*Dibenzocoronene*-3 : 4-*dicarboxylic Anhydride* (VII).—(*a*) 1 : 12-2 : 3-8 : 9-Tribenzoperylene[2] (VI) (2 g.) was refluxed in bromomaleic anhydride (40 ml.) for 2 hr. The *anhydride* (VII) which crystallised was filtered off and washed with nitrobenzene and ether, boiled with 1-methylnaphthalene (200 ml.) (to remove any starting material), filtered off (1·5 g.), and recrystallised from nitrobenzene as dark violet needles which sintered at 395°, decomposed at 440—450°, and dissolved in concentrated sulphuric acid to a brown-yellow solution (Found: C, 86·5; H, 2·9. $C_{34}H_{14}O_3$ requires C, 86·8; H, 3·0%).

(*b*) Tribenzoperylene (VI) (0·2 g.), chloranil (0·5 g.), and maleic anhydride (5 g.) were refluxed for 90 min. The mixture was diluted with warm nitrobenzene, and the anhydride (0·22 g.) filtered off and washed with nitrobenzene and ether. Purification as above yielded an identical product.

1 : 2-7 : 8-*Dibenzocoronene* (VIII).—The anhydride (VII) (0·3 g.) and soda-lime (1 g.) were ground together and heated to 350° under nitrogen for 45 min. Sublimation was carried out at 430—450°/0·08 mm. during 4 hr. The sublimate (0·13 g.) was recrystallised from 1-methylnaphthalene and resublimed in a vacuum. 1 : 2-7 : 8-*Dibenzocoronene* formed yellow needles, m. p. 496—499°, which dissolved in hot concentrated sulphuric acid to a blue-violet solution (Found: C, 95·9; H, 4·2. $C_{32}H_{16}$ requires C, 96·0; H, 4·0%).

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