

Coronaldehyde Derivatives: Reactions of Coronene. (Part II)

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Summary: Diethyl coronylidenemalonate (II), prepared from coronaldehyde, was nitrated to diethyl dinitrocoronylidenemalonate (III). Cyanocoronene (V), also prepared from coronaldehyde *via* coronaldoxime (IV), gave on hydrolysis coronenecarboxylic acid (VII). Nitration of cyanocoronene, under vigorous conditions, produced cyanopentanitrocoronene (VI) which was converted into pentanitrocoronenecarboxylic acid (VIII). This acid (VIII) was also prepared by nitrating coronenecarboxylic acid (VII) under forcing conditions.

Introduction

Existing work on coronene concerns its synthesis and mainly its physical rather than its chemical properties. Relatively few substituted coronene compounds, prepared through either direct [1-7] or indirect [8,9] methods, have been reported. The present work concerns the preparation of further polysubstituted coronene derivatives with the ultimate aim of elucidating directing influences in this ring system.

Results and Discussion

(a) Diethyl coronylidenemalonate and its Nitration

The base-catalysed condensation of coronaldehyde (I) with diethyl malonate gave diethyl coronylidenemalonate (II). Unusually amongst substituted coronenes, this compound was very soluble in low boiling solvents such as chloroform.

The nitration of (II) was attempted, following the method of Bordwell [10] by heating in acetic anhydride with

acetyl nitrate. A mixture of polynitro-derivatives of (II) resulted. Repetition of the procedure at room temperature, using the same quantities of reagents, gave analytically pure diethyl dinitrocoronylidene malonate (III).

(b) Cyanocoronene, coronenecarboxylic acid and their derivatives

The preparation of cyanocoronene from coronaldehyde was attempted by Van's method [11]. The infrared spectrum of the reaction product showed that it was largely unreacted coronaldehyde together with, perhaps, a small quantity of the nitrile. Repetition of the experiment using a ten-fold increase in the quantities of reagents and with longer heating was not successful. Cyanocoronene (V) was ultimately obtained when coronaldehyde was first converted into coronaldoxime (IV) and this oxime was heated in acetic anhydride. The product showed a very sharp and characteristic absorption at 2222 cm^{-1} in the infrared, for $\text{-C}\equiv\text{N}$ attached to an aryl ring.

Cyanocoronene was nitrated to cyanopentanitrocoronene (VI) by following the method used for acetylpentanitrocoronene and pentanitrocoronaldehyde [12]. By heating the cyanopentanitrocoronene in concentrated nitric acid (d 1.42) the cyano group was hydrolysed and pentanitrocoronenecarboxylic acid (VIII) was obtained. This compound (VIII) was also prepared by polynitration of coronenecarboxylic acid (VIII). Identification was by mixed melting point and infrared spectroscopy.

Attempts were made to hydrolyse cyanocoronene to coronenecarboxylic acid. In one attempt, the finely ground nitrile was heated in sulphuric acid (70% w/w) but the melting point and infrared absorption spectrum of the resultant product showed it to be largely unchanged cyanocoronene. Another unsuccessful attempt was made by heating cyanocoronene in a mixture of concentrated hydrochloric acid and glacial acetic acid with hydrogen chloride gas being continuously bubbled through the reaction mixture. However, coronenecarboxylic acid (VII) was finally prepared from cyanocoronene by using the method of Buu-Hoi [13]. Cyanocoronene was heated with sodium hydroxide in absolute ethanol and dry dioxan for a prolonged period.

Several attempts were made to prepare coronenecarboxylic acid by oxidation of coronaldehyde (a) with boiling aqueous alkaline potassium permanganate for 15 hours; (b) with manganese dioxide [14] in boiling xylene for 24 hours, followed by removal of the excess of manganese dioxide with sodium metabisulphite and aqueous sulphuric acid; (c) by stirring a paste of coronaldehyde and Teepol with water, sodium hydroxide and silver oxide at approximately 35° for 24 hours; and (d) by heating with silver picolinate [15] in dimethyl

sulphoxide, near to the boiling point of the solvent, for 24 hours.

In all the above attempts, the reaction product was found from a mixed melting point and the infrared spectrum to be unreacted coronaldehyde. As all these attempts at mild oxidation of coronaldehyde had failed, one attempt at vigorous oxidation was made by treating a boiling solution of the aldehyde, in nitrobenzene and glacial acetic acid, with a solution of sodium dichromate in glacial acetic acid. From the reaction mixture was isolated a dark coloured product having infrared absorption at 1660 cm^{-1} , which was indicative of coronenecarboxylic acid. However, attempts at purification unfortunately failed.

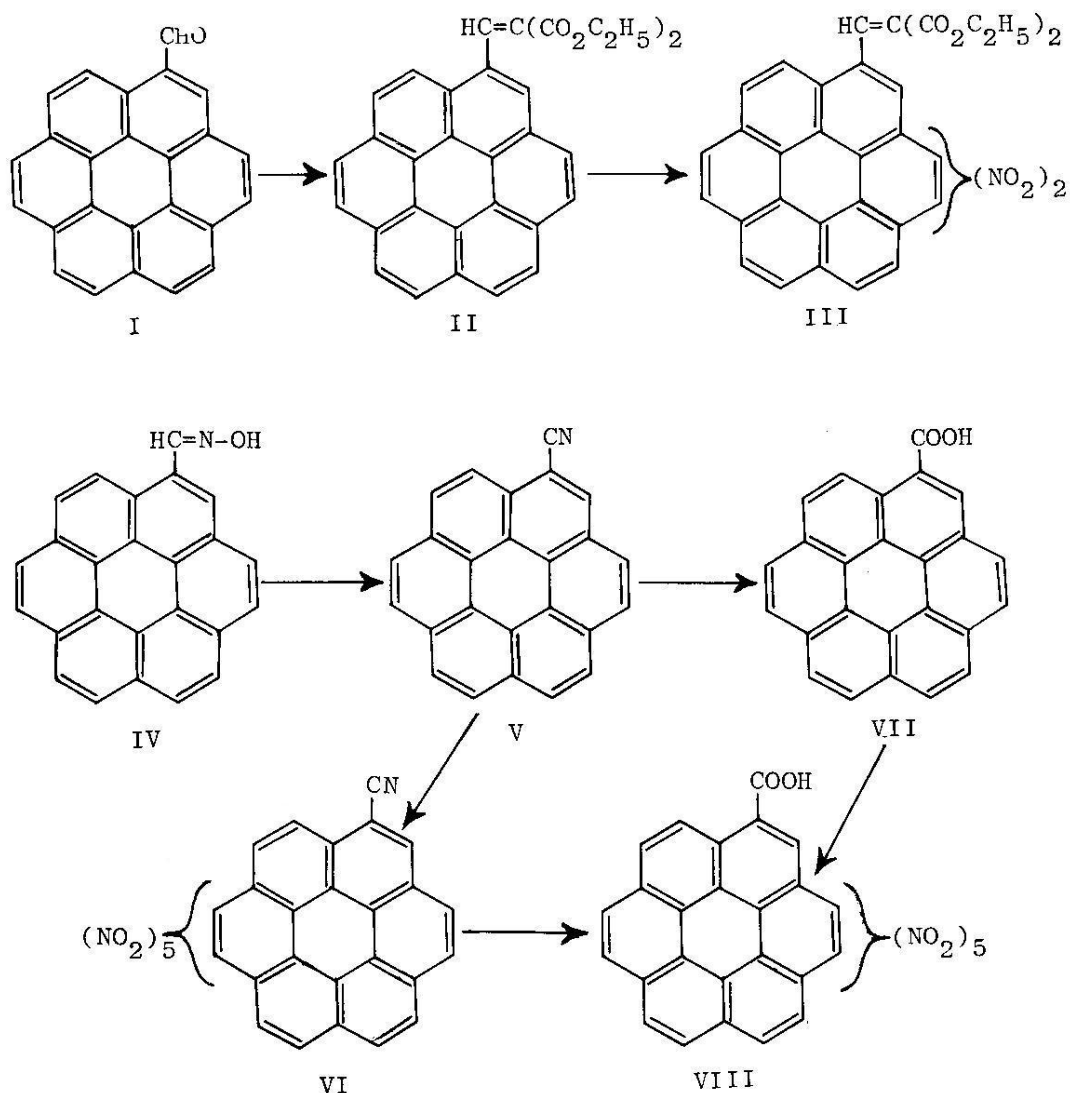
Experimental

U.V. absorption spectra are for solutions in dimethylformamide, i.r. data are for Nujol mulls, and ^1H n.m.r. were measured at 60 MHz.

Recrystallisation of some of the products proved impracticable preparations were therefore conducted under analytically clean conditions.

Coronaldehyde

A fine suspension of coronene (1.00 g) in carbon disulphide (100 ml) at 0° was treated with titanium tetrachloride (6.5 ml) and *n*-butyl dichloromethyl ether (1.5 g) with stirring. The mixture was further stirred at 0° for 1 hour and then for 15 hours at room temperature. The blue solution, so obtained, was acidified with aqueous hydrochloric acid (3M; 50 ml); the colour changed to orange-yellow. The residue was filtered off, washed successively with dilute hydro-



chloric acid, water, ammonium hydroxide, water, methanol, finally with ether, to give orange-yellow crystals (0.910 g), m.p. 339-340°. The crude product (0.910 g) was recrystallised from xylene three times to give long orange-yellow needles of coronaldehyde (0.434 g), m.p. 340-341° (literature m.p. 360°;⁵ 342°;⁶ 389°;⁷) (Found: C, 81.3; H, 3.7. Calculated for $C_{25}H_{12}O$: C, 91.4; H, 3.7%); λ_{\max} 444 nm ($\xi \times 10^{-3}$, 2.44), 419 (1.50), 379 (10.73), 339 sh (16.56), 324

(53.84), 315 (53.84), 303 (57.79), 290 sh (33.50), and 282 (25.60); ν_{\max} 2720, 1685, 1620, 1307 and 848 cm^{-1} .

The aldehyde was further characterised as the hydrazone, prepared with an excess of hydrazine hydrate in boiling pyridine. The coronaldehyde hydrazone formed fine yellow crystals, m.p. 375-376° [Literature m.p. 360° (decomp.)⁶] (Found: C, 87.5; H, 3.95; N, 8.25. Calculated for $C_{25}H_{14}N_2$: C, 87.7; H, 4.1; N, 8.2%)

Diethylcoronylidenemalonate

Ground coronaldehyde (0.251 g), pyridine (15 ml), diethyl malonate (2 ml) and piperidine (0.5 ml) were heated under reflux with stirring for 45 hours. After being cooled, the reaction mixture was acidified with aqueous hydrochloric acid (2M; 40 ml); a brown solid separated. The reaction mixture was then diluted with water (20 ml) and the solid was filtered off, washed with water and with light petroleum (b.p. 40-60°) and dried to give diethylcoronylidenemalonate (0.328 g), m.p. 128-129° (Found: C, 81.8; H, 4.65. $C_{32}H_{22}O_4$ requires C, 81.7; H, 4.7%); m/e 470; λ_{max} 380 nm sh ($\xi \times 10^{-3}$, 9.25), 343 (27.77), 322 sh (51.19), 307 (89.32), 295 sh (48.47); ν_{max} 1725, 1620, 1318, 1308, 1265, 1235, 1222, 1205, 1065 and 845 cm^{-1} . δ ($CDCl_3$) 8.12 (1H, s, olefinic H), 8.32 (1H, m, aromatic H), 4.55 and 4.12 (each 2H, quartet, CH_2-CH_3), 8.46 and 9.08 (each 3H, triplet, CH_2-CH_3).

Diethyl Dinitrocoronylidenemalonate

A solution of diethyl coronylidenemalonate (0.50 g) in acetic anhydride (50 ml) was added at room temperature, with stirring to a solution of acetyl nitrate [prepared by the addition of concentrated nitric acid (d 1.42; 1ml) at room temperature to acetic anhydride (7 ml) over a period of 1 minute, the temperature of the reaction mixture being maintained at 30-35° using a mixture of dry ice and methanol)]. The reaction mixture was stirred for a further 8 hours, then poured into ice-cold water, and the resulting solution, containing green coloured oily drops, was induced to crystallise by trituration. The greenish-brown solid was filtered off, washed

with water and light petroleum b.p. 40-60°, and dried. After recrystallisation from acetic acid, diethyl dinitrocoronylidenemalonate (0.57 g), formed fine yellow needles, m.p. 166-168° (Found: C, 68.4; H, 3.25, N, 5.0 $C_{32}H_{20}N_2O_8$ requires C, 68.7; H, 3.4; N, 5.0%); λ_{max} 460 nm $\xi \times 10^{-3}$, 2.58), 406 sh (11.21), 360 sh (31.91) and 312 (42.25); ν_{max} 1725, 1619, 1528, 1385, 1342, 1310, 1300, 1264, 1242, 1215 and 845 cm^{-1} .

Coronaldoxime

Ground coronaldehyde (0.25 g) and hydroxylamine hydrochloride (12.0 g) were heated, under reflux, in pyridine (20 ml), and during 30 minutes sodium carbonate (5.0 g) was added in portions. Effervescence occurred and the reaction mixture was then heated, under reflux, for 1 hour. Distilled water (approximately 60 ml) was added to the hot solution causing very fine light-yellow needles to separate. This mixture was allowed to cool and then to stand for 15 hours. The resulting solid was washed with water, methanol and ether, and was dried (yield, 0.218 g, m.p. 303-305°). Recrystallisation from industrial methylated spirits gave fine pale-yellow needles of coronaldoxime (0.201 g), m.p. 304-306° (Found C, 87.8, H, 3.75; N, 4.1 $C_{25}H_{13}NO$ requires C, 87.7; H, 3.8; N, 4.05%); λ_{max} 438 nm ($\xi \times 10^{-3}$, 1.12), 413 (1.12), 370 (14.81), 342 (21.09), 320 sh (84.38), 308 (93.35), and 294 sh (37.70); ν_{max} 3290, 1615, 950, and 845 cm^{-1} .

Cyanocoronene

Ground coronaldoxime (0.172 g) was heated, under reflux, with

stirring for 15 hours in acetic anhydride (20 ml). The brownish-yellow solid was filtered off, washed with water and methanol, and finally with ether, and was dried. The reaction product (0.142 g) had m.p. 440-444°. Recrystallisation from xylene (90 ml for 0.134 g) gave brown needles of cyanocoronene (0.087 g), m.p. 440-442° (Found: C, 92.1; H, 3.5 N, 4.2. $C_{25}H_{11}N$ requires C, 92.3; H, 3.4; N, 4.3%); λ_{\max} 435 nm ($\xi \times 10^{-3}$, 3.30), 411 (1.94), 389 (1.16), 368 (11.28), 349 (16.34), 338 (15.95), 320 (47.87), 311 (72.01), 304 (59.16) and 280 sh (16.34); ν_{\max} 2222, 1620, 1316 and 846 cm^{-1} .

Cyanopentanitrocoronene

To a suspension of ground cyanocoronene (0.158 g) in carbon tetrachloride (6 ml) was added fuming nitric acid (d 1.5; 4 ml) dropwise and with constant shaking and cooling. After being shaken for 2 hours, at room temperature, the reaction solution was poured into a large volume of water and the carbon tetrachloride was removed under reduced pressure. The brown solid was filtered off, washed with water, methanol and with ether, and was dried to give cyanopentanitrocoronene (0.246 g), m.p. 362-368° (decomp.) (Found: C, 54.4; H, 1.25; N, 15.15. $C_{25}H_6N_6O_{10}$ requires C, 54.6; H, 1.1; N, 15.25%); λ_{\max} 570 nm ($\xi \times 10^{-3}$, 1.44), 460 (2.88), 433 (4.32), 400 sh (12.98), 382 sh (19.24) and 344 (52.91); ν_{\max} 2245, 1628, 1548, 1360, 915, and 808 cm^{-1} .

Pentanitrocoronene-carboxylic Acid

(a) Ground cyanopentanitrocoronene (0.276 g) was heated under

reflux with stirring in concentrated nitric acid (d 1.42; 25 ml) for 20 hours. The reaction mixture was allowed to attain room temperature, and then poured into a large volume of water; there separated very fine, brown crystals which were collected, washed with water and light petroleum (b.p. 40-60°), and dried to give pentanitrocoronene-carboxylic acid (0.177 g), m.p. 318-320° (decomp.) (Found: C, 52.6; H, 1.35; N, 12.5. $C_{25}H_7N_5O_{12}$ requires C, 52.7; H, 1.25; N, 12.3%); λ_{\max} 580 nm ($\xi \times 10^{-3}$, 1.33), 470 (4.0), 407 sh (11.56) and 348 (41.81); ν_{\max} 3070, 1720, 1625, 1540, 1352, 915 and 812 cm^{-1} .

(b) Fuming nitric acid (d 1.5; 3.5 ml) was added in small portions to suspension of ground coronene-carboxylic acid (0.17 g) in carbon tetrachloride (6 ml), with constant shaking, swirling, and intermittent cooling. On addition of the first few drops of nitric acid the solid compound turned black; with the complete addition of the acid, the reaction mixture separated into two layers. The mixture was shaken for 5 hours at room temperature and poured into a large volume of water; the carbon tetrachloride layer was then removed under reduced pressure. The product was collected and washed with water and light petroleum (b.p. 40-60°), to afford a reddish-brown solid (0.314 g). This product was pentanitrocoronene-carboxylic acid because it decomposed at 318-320° both alone and when mixed with an authentic sample of pentanitrocoronene-carboxylic acid (Found: C, 52.8; H, 1.4; N, 12.0. Calculated for $C_{25}H_7N_5O_{12}$: C, 52.7; H, 1.25; N, 12.3%); ν_{\max} 1720, 1535, 1350 and 810 cm^{-1} .

Coronenecarboxylic Acid

A mixture of ground cyanocoronene (0.252 g), sodium hydroxide (0.5 g), absolute ethanol (15 ml), and dry dioxan (15 ml) was heated, under reflux, with stirring for 72 hours. The ethanol was removed under reduced pressure and water (approximately 15 ml) was added. The resulting light-yellow solid was filtered off, washed with boiling benzene (approximately 15 ml) and ether, and then dried. The product was then made into a suspension in water (20 ml) and aqueous hydrochloric acid (3M; 25 ml) was added to give very fine pale yellow needles. The solid was filtered off, washed with water, methanol, and ether, and then dried. The crude reaction product (0.245 g), m.p. 340-342°, was recrystallised twice from nitrobenzene (25 ml) to give fine pale yellow needles of coronene-carboxylic acid, m.p. 341-342° (Literature m.p. 341°)⁴. (Found: C, 87.2; H, 3.5. Calculated for C₂₅H₁₂O₂: C, 87.5; H, 3.45%); λ_{\max} 435 nm ($\xi \times 10^{-3}$, 0.64), 411 (0.64), 343 (25.69), 320.5 sh (27.67), 307 (119.86), and 295 sh (57.36); ν_{\max} 3360, 3170, 1690, 1620, 1275 and 848 cm⁻¹.

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