NOTES *Bull. Chem. Soc. Jpn.*, *55*, 3933—3934 (1982)

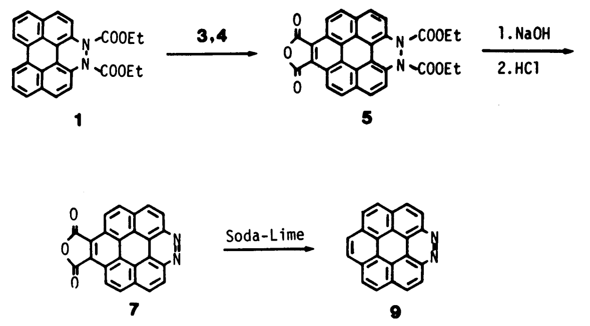
The Synthesis of 1,2-Diazacoronene

Sumio Tokita,* Kimihiro Hiruta, Kiyoshi Kitahara, and Hisao Nishi
Department of Applied Chemistry, Faculty of Engineering, Saitama University,
Shimo-Ohkubo, Urawa, Saitama 338

(Received December 10, 1981)

Synopsis. 1,2-Bis(ethoxycarbonyl)-1,2-dihydro-1,2-diazacoronene-7,8-dicarboxylic anhydride (5) was obtained from diethyl 1,2-dihydro-1,2-diazabenzo[*ghi*]perylene-1,2-dicarboxylate, maleic anhydride, and chloranil. Treatment of the anhydride 5 with sodium hydroxide gave 1,2-diazacoronene-7,8-dicarboxylic anhydride (7). When 7 was heated with soda lime, 1,2-diazacoronene was obtained.

Much attention is being given to the heterocyclic analogs of highly annelated polycyclic hydrocarbons found in urban suspended particulate matter, especially to the compounds suspected of tumorigenic activities. There are, however, few reports about the synthesis of authentic samples of highly annelated heterocycles, in spite of the existence of many reports on heterocyclic analogs of benzene,[1–3)] naphthalene,[1–3)] anthracene,[2,4)] or phenanthrene.[3,4)] In the case of nitrogen heterocyclic analogs of coronene, only 1,2,7,8-tetraazacoronene has been synthesized.[5)] The preparation of 1,2-diazacoronene (**9**), however, proved to be more difficult.[5)] Thus, the attempted Diels-Alder reaction of benzo[*ghi*]perylene with diethyl azodiformate (**2**) did not give any diethyl 1,2-dihydro-1,2-diazacoronene-1,2-dicarboxylate, a precursor of **9**. This paper deals with the synthesis of **9** by another route.

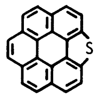


When diethyl 1,2-dihydro-1,2-diazabenzo[*ghi*]perylene-1,2-dicarboxylate (**1**) was treated with maleic anhydride (**3**) in the presence of chloranil (**4**), the expected adduct, 1,2-bis(ethoxycarbonyl)-1,2-dihydro-1,2-diazacoronene-7,8-dicarboxylic anhydride (**5**) was obtained in fair yield. But the treatment of benzo[*ghi*]perylene-1,2-dicarboxylic anhydride (**6**) with **2** in an autoclave at 160 °C for 144 h did not result in the formation of **5** but in the recovery of **6**.

Hydrolysis of the anhydride **5** with sodium hydroxide followed by acidification gave 1,2-diazacoronene-7,8-dicarboxylic anhydride (**7**) almost quantitatively. The reaction of 1,2-diazabenzo[*ghi*]perylene (**8**) with **3** in the presence of **4** at 200 °C for 20 min gave a very complex mixture, in which **7** could not be detected.

1,2-Diazacoronene (**9**) was prepared by the action of soda lime on anhydride **7**. On the other hand, the reaction of **5** with the same reagent at 280—300 °C for 2 h gave a dark solid from which no definite products could be isolated.

1,2-Diazacoronene (**9**) was soluble in trifluoroacetic acid and bis(2-hydroxyethyl) ether, whereas it was almost insoluble in common organic solvents. It could be recrystallized from bis(2-hydroxyethyl) ether in fine needles. It is yellow with a considerably deeper shade than coronene. The electronic spectrum of **9** (see experimental section) and that of coronene[6,7)] were quite similar with respect to the positions of absorption maxima, but differ in that the absorption band of **9** in the visible region has a higher intensity ($\varepsilon \approx 10^4$) than that of coronene ($\varepsilon \approx 10^2$). These findings may be accounted for by the same symmetry argument that explains the difference between the spectra of benzene and pyridine.[8)] Incidentaly, the electronic spectrum of an analogous isoelectronic compound, *viz.*, benzo[6,7]perylo[1,12-*bcd*]thiophene (**10**),[9)] shows essentially the same characteristics as **9**.



10

The NMR spectrum of **9** was as expected. In **9**, there were aromatic proton signals at lower field than in coronene, and at higher field than in 1,2,7,8-tetraazacoronene.[5)]

Experimental

^{1}H NMR spectra were recorded on a Varian Model A-60 Spectrometer in CF_3COOH using Me_4Si as an internal standard. IR spectra were recorded on a JASCO Model A-3 grating spectrophotometer using the KBr technique. Mass spectra were obtained on a JEOL JMS-01-SG-2 spectrometer at an ionization potential of 35 eV. Electronic spectra were measured with a Hitachi EPS-3T recording spectrophotometer.

Materials. Diethyl azodiformate (**2**)[10)] and benzo[*ghi*]perylene-1,2-dicarboxylic anhydride (**6**)[6)] were prepared and purified according to the procedures in the literature. Diethyl 1,2-dihydro-1,2-diazabenzo[*ghi*]perylene-1,2-dicarboxylate (**1**) and 1,2-diazabenzo[*ghi*]perylene (**8**) were prepared and purified by the methods reported previously.[5)]

1,2-(Bis(ethoxycarbonyl)-1,2-dihydro-1,2-diazacoronene-7,8-dicarboxylic Anhydride (5). A mixture of **1** (212 mg, 0.50 mmol), chloranil (**4**, 369 mg, 1.50 mmol), and maleic anhydride (**3**, 1.45 g, 15 mmol) was heated under reflux for 20 min. The reaction mixture was then allowed to cool to about 80 °C, and 2 ml of xylene was added. After cooling, 10 ml of methanol was added and the resulting precipitate was filtered off to give 205 mg of crude **5**. Recrystallization from xylene afforded 158 mg of **5** as a reddish brown solid (61% yield): mp 305 °C (decomp); IR 3000 (ν_{C-H}^{arom}), 2950 (ν_{C-H}^{aliph}), 1840 ($\nu_{C=O}$), 1765 ($\nu_{C=O}$), 1730 ($\nu_{C=O}$), 1325 (ν_{C-O}), 1260 (ν_{C-O}), 845 cm^{-1} (δ_{C-H}); ^{1}H NMR δ 1.54 (t, 6H, J=7.3 Hz), 4.60 (q, 4H, J=7.3 Hz), 6.78 (d, 2H, J=9.1 Hz), 7.22 (d, 2H, J=9.1 Hz), 7.89 (d, 2H, J=8.8 Hz), 8.22 (d, 2H, J=8.8 Hz); MS m/e 518 (7%, M$^+$), 446 (10%), 445 (26%), 401 (20%), 373 (100%). Found: C, 69.93; H, 3.37; N, 5.73%. Calcd for $C_{30}H_{18}N_2O_7$: C, 69.49; H, 3.51; N, 5.40%.

1,2-Diazacoronene-7,8-dicarboxylic Anhydride (7). To a stirred benzyl alcohol (30 ml) solution of **5** (104 mg, 0.20 mmol) at 100 °C, sodium hydroxide pellets (93% pure, 260 mg, 6 mmol) were added in one portion. The stirring was continued at this temperature for 30 min. After cooling, the reaction mixture was acidified with concentrated hydrochloric acid. Evaporation of the mixture and trituration of the residue with methanol followed by filtration gave crude **7**, 74 mg (99%). Recrystallization from nitrobenzene or sublimation at 330—350 °C/20 mmHg[†] for 5 h gave yellowish brown fine needles of pure **7** (59% or 70% yield respectively): mp 400 °C (decomp); IR 3100 (ν_{C-H}^{arom}), 1840 ($\nu_{C=O}$), 1765 ($\nu_{C=O}$), 1290 (ν_{C-O}), 850 cm^{-1} (δ_{C-H}); ^{1}H NMR δ 9.68 (d, 2H, J=8.8 Hz), 9.72 (m, 4H), 10.52 (d, 2H, J=8.8 Hz); MS m/e 372 (70%, M$^+$), 300 (65%), 272 (100%). Found: C, 77.30; H, 2.04; N, 7.28%. Calcd for $C_{24}H_8N_2O_3$: C, 77.41; H, 2.17; N, 7.53%.

1,2-Diazacoronene (9). Anhydride **7** (75.6 mg, 0.20 mmol) and soda lime (300 mg, Wako Pure Chemical Industries Ltd.) were powdered together and heated in a sublimation apparatus at 320 °C for 1 h. The apparatus was then evacuated (20 mmHg) and the temperature raised to 350 °C for 2 h. The sublimate (24 mg), recrystallized from bis(2-hydroxyethyl)ether, gave 1,2-diazacoronene in pale yellow needles, 16 mg (26% yield): mp 468—470 °C (decomp); IR 3060 (ν_{C-H}^{arom}), 850 cm^{-1} (δ_{C-H}); ^{1}H NMR δ 8.62 (s, 2H), 8.82 (d, 2H, J=9.0 Hz), 8.91 (d, 2H, J=9.0 Hz), 9.10 (m, 4H); MS m/e 302 (74%, M$^+$), 274 (76%), 137 (100%); UV (in C_6H_6) λ_{max} (log ε) 437 (3.89), 413 (3.62), 321 (4.79), 308 (4.64). Found: C, 87.34; H, 3.14; N, 9.53%. Calcd for $C_{22}H_{10}N_2$: C, 87.39; H, 3.34; N, 9.27%.

The authors wish to express their sincere thanks to Emeritus Professor Osamu Simamura for the correction of this manuscript.

References

1) "Rodd's Chemistry of Carbon Compounds," ed by S. Coffey, Elsevier Scientific Publishing Co., Amsterdam (1976), Vol. IV, Part F.

2) "Heterocyclic Compounds," ed by R. C. Elderfield John Wiley and Sons, Inc., London (1957), Vol. 6.

3) "Heterocyclic Compounds," ed by R. C. Elderfield, John Wiley and Sons, Inc., London (1961), Vol. 7.

4) "Rodd's Chemistry of Carbon Compounds," ed by S. Coffey, Elsevier Scientific Publishing Co., Amsterdam (1978), Vol. IV, Part G.

5) S. Tokita, K. Hiruta, K. Kitahara, and H. Nishi, *Synthesis*, **1982**, 229.

6) E. Clar and M. Zander, *J. Chem. Soc.*, **1957**, 4616.

7) E. Clar, "Polycyclic Hydrocarbons," Academic Press, London (1964), p. 83.

8) H. H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York (1962), p. 361.

9) J. H. Dopper and H. Wynberg, *J. Org. Chem.*, **40**, 1957 (1975).

10) J. C. Kauer, *Org. Synth.*, Coll. Vol. IV, 411 (1963).

[†] 1 mmHg=133.322 Pa.