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Syntheses of Diphenic Anhydride-Mercury Compounds and Their Reaction with Nucleophilic Reagents

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Diphenic acid anhydride (**1**) is decarbonylated by prolonged heating with mercuric oxide (HgO) in acetic acid to give a diphenic anhydride-mercury compound (**3**). Since its infrared spectrum showed a shift of carbonyl adsorption to a very low wave number, the O-Hg linkage was considered to be in an ionic form (**3'**), with the carbon bonded to mercury becoming a carbonium ion. If this is the case, the compound would be expected to react with nucleophilic reagents and indeed **3** is reactive to KI, H_2S and KCN.

Keywords——diphenic anhydride-mercury compound; mercuration; carbon-mercury bond; carbonyl adsorptions; nucleophilic; the reaction mechanism; protonation

Whitmore and Culhame[1] synthesized phthalic anhydridemercury compound in which the mercury is directly bonded to the benzene ring from phthalic acid and mercury acetate.

One of the authors has reported syntheses of a naphthalic anhydride-mercury compound,[2] a heterocyclic pyridine-3-carboxylic compound[3] and an aliphatic norbornene anhydride-mercury compound,[4] and showed that nucleophilic displacement occurs at the C–Hg bonds. The present study reports the synthesis and the nucleophilic displacement reaction of a diphenic anhydride-mercury compound.

Experiments on the mercuration of diphenic acid anhydride showed that a diphenic anhydride-mercury compound (**3**), in which an aromatic ring is directly mercurized, is obtained by adding an acetic acid solution of mercuric oxide to a sodium hydroxide solution of diphenic anhydride, and refluxing the mixture for 20 hours at pH=5.0—5.8 and at temperatures of 130—140°C. Compound **3** is barely soluble in water and organic solvents, and is stable in air.

The structure of **3** was deduced from the elementary analysis, an atomic absorption peak of mercury at 2537 Å and a mass spectrum that shows $m/e=396$ (M^+).

Compound **3**, when dissolved in sodium hydroxide and treated with hydrochloric acid at an ambient temperature, gives **4**. Its structure was determined by elementary analysis, the mass spectrum that showed an m/e value of about 432.5 (M^+) and the IR absorption at 1560 cm^{-1} due to –COOH group. The infrared absorption spectra are characterized by peaks remarkably shifted to lower wave numbers, as in the case of the carboxylic groups in naphtho-[1,8-*c*,*d*][1,2] oxamercuric-3-one (1530 cm^{-1}), pyridine-2-mercuric-3-carboxylic anhydride (1580 cm^{-1}) and 3-mercuri-5-norbornene-2-carboxylic anhydride (1545 cm^{-1}). This suggests a strong carboxylate character of the carbonyl group, and thus a considerable ionic character of the O–Hg bond. The reactions of the diphenic anhydride-mercury compound with nucleophilic reagents were investigated as follows.

(1) The Reaction with Halogens

Potassium iodide was added to the diphenic anhydride-mercury compound in glacial acetic acid in the presence of water. The compound was readily dissolved when the flask was shaken. High speed liquid chromatography showed that the reaction product was a mixture of two compounds, **5**[9] and **6**, which were separated by silica gel chromatography with benzene–acetone (1 : 1) mixture. An empirical formula $C_{13}H_9O_2I$ for **5** was derived from elementary analysis; the structure was deduced from the results of mass spectroscopy, which gave $m/e=324$ (M^+), and the infrared absorption by –COOH group at 1685 cm^{-1}. Although nuclear magnetic resonance (NMR) spectroscopy (DMSO-d_6) did not show any proton signal due to the –COOH group, 5 was positive in the Beilstein reaction. Compound **6**[5–8] was identified from its infrared, NMR and mass spectra, which were identical with those of a standard specimen (Chart 2).

(2) The Reaction with Hydrogen Sulfide

The reaction of **3** with hydrogen sulfide in glacial acetic acid in the presence of water gave the 2′-thio derivative (**7**) and 1,1′-biphenyl-2-carboxylic acid (**6**).[10] A broad singlet signal at $\delta=9.2$ ppm in the NMR spectrum was assigned to the proton in the thio group; this signal disappeared in the presence of D_2O. The infrared (IR) spectrum showed assorptions at 2080 cm^{-1} and 1690 cm^{-1} due to the –SH and –COOH groups. respectively. 1,1′-Biphenyl-2-carboxylic acid (**6**) was identified as above.

(3) The Reaction with Cyanide Ion

The similar reaction of 3 with hydrogen cyanide did not give a 2′-cyano derivative, but gave an aldehyde (**8**)[11,12] and 1,1′-biphenyl-2-carboxylic acid (**6**). Compound **8** has the empirical formula $C_{14}H_{10}O_3$; a singlet signal at $\delta=10.4$ ppm in the NMR spectrum was assigned to the proton in the aldehyde group. No signal was observed for the proton in the –COOH group. The IR spectrum showed carbonyl adsorptions at 1695 cm^{-1} and 1685 cm^{-1} due to the –CHO and –COOH groups, respectively. The mass spectrum gave $m/e=226$ (M^+). These observations, together with the fact that its oxidation with potassium bichromate ($K_2Cr_2O_7$) yields biphenyl-2,2′-dicarbooxylic acid, permitted determination of the structure of **8**. 1,1′-Biphenyl-2-carboxylic acid (**6**) was identified as above. A plausible reaction mechanism for the formation of these compounds is shown in Chart 3.

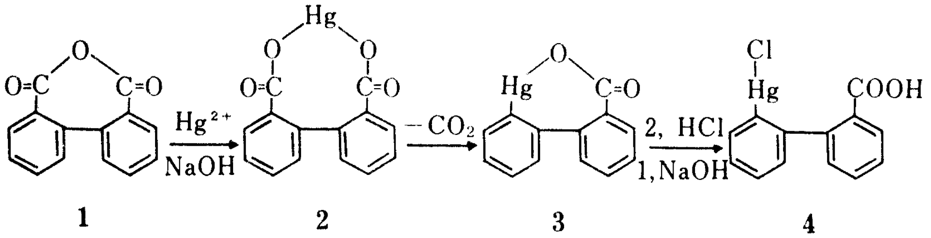

Chart 1

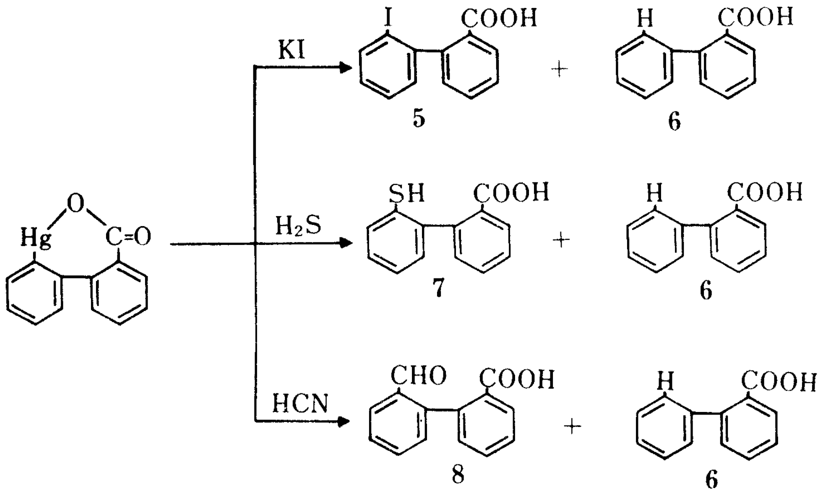

Chart 2

Discussion

The strong carboxylate character of the carboxylic group in the diphenic anhydridemercury compound suggests that the O–Hg bond is highly polarized, contrary to the usual assumption that it is similar to a δ-bond. A resonance structure (**3′**) involving a polarized structure with a cationic mercury atom may be important. This suggests a dual reactivity of the aromatic ring directly bonded to Hg^+: it is expected to be reactive with electrophilic reagents when Hg^+ is oxidized to Hg^{2+} through the carbon-mercury bond (C–Hg), and to be reactive with nucleophilic reagents when Hg^+ is reduced to Hgo. The reaction shown in Chart 3 gives an aldehyde (**10**) *via* route A, but does not give a nitrile. An electrophilic displacement (protonation) occurs simultaneously *via* route B.

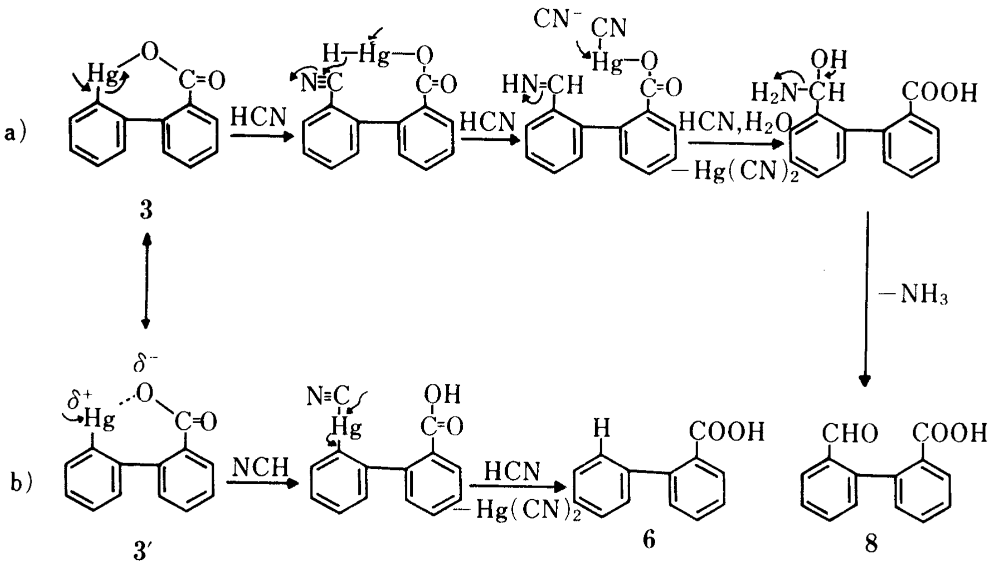

Chart 3

Experimental

Mercuration of Diphenic Anhydride——A solution of 4.9 g (0.023 mol) of HgO dissolved in a mixture of 15 ml of glacial AcOH and 50 ml of H_2O was added to a solution of 5.0 g (0.022 mol) of diphenic anhydride dissolved in 30 ml of 5% NaOH solution with stirring, the pH was adjusted to 5.0—5.8, and the mixture was refluxed at 130—140°C for *ca.* 20 h. CO_2 evolved during the refluxing was absorbed in $Ba(OH)_2$ solution and the refluxing was continued until the $Ba(OH)_2$ solution no longer became turbid.

The refluxed solution was filtered while hot then the solid was washed with glacial AcOH and H_2O, dried, and washed with MeOH, affording 8.1 g of fine white crystals, mp >300°C. MS *m/e*: 396 (M^+). *Anal.* Calcd for $C_{13}H_8HgO_2$: C, 39.39; H, 2.02. Found: C, 39.61; H, 2.06.

Detection of Hg in the Product: A a) X-Ray Intensity Method: A GF-S (Hitachi) apparatus was used, and the spectrum was obtained under a pressure of 25 t/40. The value obtained was 35600 cps at 30 kW, 10 mA. b) Atomic Absorption Photometry: The apparatus used was a Hitachi spectrophotometer, model 207. The sample was dissolved in 50% AcOH to saturation, and the absorption was measured at 2537 Å.

Reaction with Diphenic-mercuric Acid Anhydride and Potassium Iodide——One gram of KI was added to 1.0 g (0.0025 mol) of diphenic mercuric acid anhydride (**3**) suspended in a mixture of 20 ml of glacial AcOH and 1.0 ml of H_2O, and the mixture was shaken vigorously at room temperature until the reactants dissolved completely. The mixture was allowed to stand for *ca.* 48 h, then the solvent was evaporated off under reduced pressure. The residue was extracted with acetic acid ethyl ester. The extract was concentrated from acetic acid ethyl ester. The reaction mixture was centrifuged to separate a precipitate (350 mg), which was purified by column chromatography (silica gel with benzene–acetone = 1: 1) to provide 100 mg of **5**, yield 37%, mp 149—153°C. The residue left after extraction with acetic acid ethyl ester was recrystallized from acetone to give 150 mg of **6**, yield 13%, mp 114—116°C. *Anal.* Calcd for $C_{13}H_{10}IO_2$: C, 48.30; H, 2.77. Found: C, 48.58; H, 2.68. IR ν_{max}^{KBr} cm^{-1} 1685 (–COOH), NMR (DMSO-d_6) δ = 7—8 ppm 8H (arom. ring). MS *m/e*: 324 (M^+). 1,1′-Biphenyl-2-carboxylic acid (**6**): *Anal.* Calcd for $C_{13}H_{10}O_2$: C, 78.79; H, 5.50. Found: 78.84; H, 5.23. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1} 1680 (-COOH). MS *m/e*: 198 (M$^+$) ^{1}H-NMR (DMSO-d_6) δ=7.8 ppm 9H (arom. ring).

Reaction with Diphenic-mercuric Acid Anhydride and Hydrogen Cyanide——Hydrogen cyanide was bubbled through a suspension of 1.0 g (0.0025 mmol) diphenic-mercuric acid anhydride (3) in a mixture of 20 ml of glacial acetic acid and 1.0 ml water. The mixture was allowed to stand for *ca.* 50 h, then the solvent was evaporated off under reduced pressure. The residue was extracted with acetic acid ethyl ester and the residue was recrystallized from the same solvent to give 200 mg of **8**, yield 35.5%, mp 135—138°C. The residue left after extraction with acetic acid ethyl ester was recrystallized from acetone give 100 mg of **6**, yield 20.0%, mp 114—116°C. *Anal.* Calcd for $C_{14}H_{10}O_3$: C, 74.34; H, 4.46. Found: C, 74.55; H, 4.66. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1} 1695 (-CHO), 1685 (-COOH). ^{1}H-NMR (DMSO-d_6) δ=10.4 ppm (-CHO), ^{13}C-NMR (DMSO-d_6) δ=191.4 ppm (-CHO). MS *m/e*: 226 (M$^+$).

2′-Thio-1,1′-biphenyl-2-carboxylic Acid (7)——Hydrogen sulfide was bubbled through a suspension of 1.0 g of 3 in a mixture of 20 ml of glacial acetic acid and 1.0 ml of water. Formation of a black precipitate of hydrogen sulfide was complete within *ca.* 20 min, but hydrogen sulfide was bubbled through for a further 10 min. HgS was removed by filtration, the filtrate was concentrated under reduced pressure, and the residue was extracted with benzene. The residue from the extract was recrystallized from acetic acid ethyl ester to give 150 mg of 7, yield 25.8%, mp 134—137°C. (7): *Anal.* Calcd for $C_{13}H_{10}O_2S$: C, 67.83; H, 4.35; S, 13.91. Found: C, 68.21; H, 4.66; S, 14.21. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1} 2080 (-SH), 1690 (-C=O). NMR (CD_3COCD_3) δ=9.2 ppm (1H, br s, -SH, 1H, br s, -COOH). MS *m/e*: 230 (M$^+$).

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