[Chem. Pharm. Bull. 27(4) 870—873 (1979)]

UDC 547.469.04 : 546.221.04

Synthesis of Norbornene Anhydride-Mercury Compound and Its Nucleophilic Reaction

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(Received August 11, 1978)

5-Norbornene anhydride–mercury compound (III) was synthesized. Since its infrared spectrum showed the shift of carbonyl absorption to a very low wave number side, O–Hg linkage was considered to be in an ionic form (III′), with the carbon in the bonded to mercury becoming a carbonium ion, suggesting the likelihood of its reaction with nucleophilic reagents.

Reactions of III with nucleophilic reagents showed that III is reactive to H_2S, KI, and KCN.

Keywords——norbornene dicarboxylic acid; norbornene anhydride–mercury compound; mercuration; carbon–mercury bond; carboxylate; polarization; nucelophilic reaction

Synthesis of naphthalic anhydride–mercury compound (VIII) with a carbon–mercury bond in the aromatic ring was reported earlier.[2] In the present series, examinations were made on compounds other than the aromatic ring, *i.e.*, norbornene derivatives. As a result, in addition to the mercury compounds of naphthalic anhydride (VIII), 3-mercuri-5-norbornene-2-carboxylic anhydride (III) was obtained by the reaction of mercuic oxide with 5-norbornene-2,3-dicarboxylic anhydride (I) in acetic acid.

Mercuration of I by the same method[3] as used for the synthesis of naphthalic anhydride–mercury compound (VIII) was examined and it was found that the addition of acetic acid solution of mercuric oxide to the aqueous NaOH solution of I and refluxing of this mixture at pH 5.0—5.7 for a long period of time resulted in the formation of amercury compound (III), with mercury bonded to the carbon in 3-position after decarboxylation of the carboxyl in 3-position. III is sparingly soluble in water and organic solvents and is stable in air.

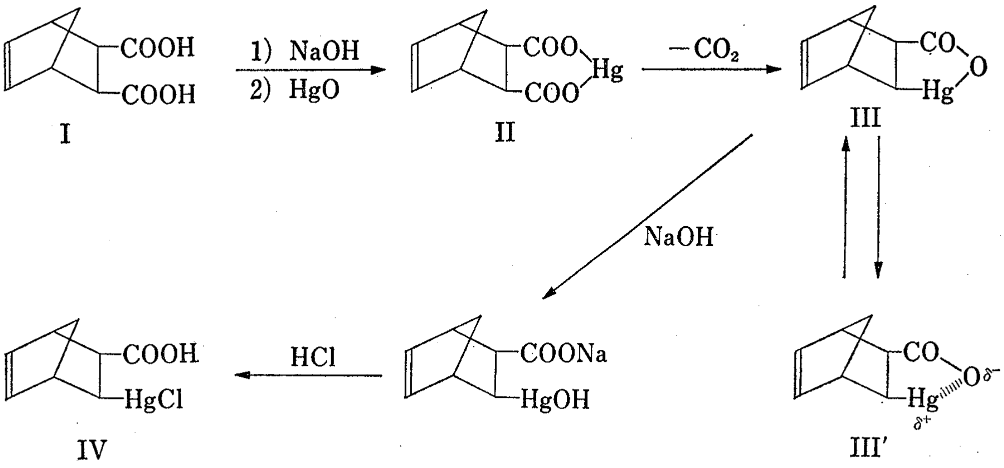

Chart 1

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[1] Location: *2-2-1 Miyama, Funabashi, Chiba-Ken 274, Japan.*

[2] T. Takahashi, *Yakugaku Zasshi*, **98**, 358 (1978).

[3] F.C. Whitmore and P.J. Culhame, *J. Am. Chem. Soc.*, **51**, 602 (1926).

Elemental analytical values of III suggested its structure III′. Detection of mercury was made by the X-ray intensity method, and mercury at 35600 cps and the presence of a peak at 2537 Å the absorption wavelength of mercury in atomic absorption photometry the intermolecular presence of mercury in III.

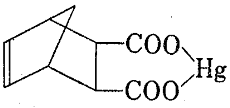
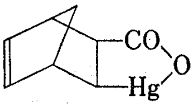
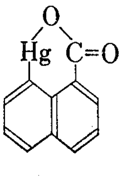
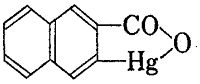
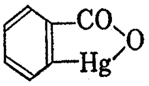
III was dissolved in sodium hydroxide solution, and treatment of this solution with hydrochloric acid solution, and gave 3-chloromercuri-2-carboxy-5-norbornene (IV). Nuclear magnetic resonance (NMR) spectrum of IV showed the signals of 2-H and 3-H at δ 3.0 and 3.1 ppm (J=5.0 and 3.5 Hz) as doublets.

Since the signals of 2-H and 3-H in the starting I appear as a doublet at 3.66 ppm (J=4.0 Hz), it is certain that different substituents are present in 2- and 3-position.

Taken together with the result of afore-mentioned X-ray intensity method and atomic absorption photometry, the structure of III was found to be represented as show in Chart 1.

For the sake of reference, absorption of the carbonyl in the infrared (IR) spectra of the previously reported mercury compounds[2] VIII, IX, and X, are listed in Table I.

Table I. IR Spectra of Carboxylic Acid Mercuri Anhydride Compounds

Compounds		IR (in KBr) $\nu_{C=O}$ (cm^{-1})
II		1580
III		1545
VIII		1530
IX		1620
X		1600

The most characteristic point in the IR spectrum of III is that the carbonyl absorption has shifted to a markedly lower were number side, in the same way as in those of VIII, IX, and X.

In other words, the nature of carbonyls is highly like a carboxylate, and the O–Hg bond seems to have an ionic nature.

Polarization of O–Hg in norbornene is assumed to be very marked.

Consequently, III may take the structure of III′.

In order to examine to what extent this difference will appear actually in some reactions of III with nucleophilic reagents were carried out.

In the reaction of III with hydrogen sulfide, III was suspended in glacial acetic acid and hydrogen sulfide gas was passed through the suspension at room temperature.

This resulted in exchange of SH group with mercury, with further oxidation, and compound (V) was formed with formation of a dithio linkage. Reaction of III with cyano ion to give a compound with cyano group directly substituted into III and an acid amide-type compound (VII) was not obtained.

These reaction mechanisms are illustrated in Chart 2.

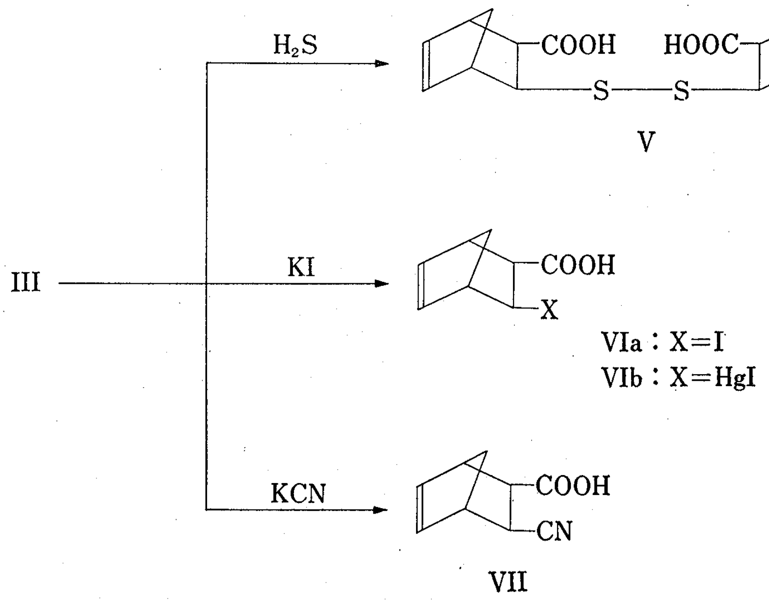


Chart 2

Reaction of III with potassium iodide gave VIa in a low yield and the main product was VIb. In these reactions, formation of 5-norbornene-2-carboxylic acid, with substitution of mercury in III with hydrogen, was not detected.

Larock and others[4,5] reported the reaction of olefinic double bond with mercury, and the reactivity of the double bond of 5-norbornene with mercury salts will be reported at a later data.

Experimental

Mercuration of Norbornene——A solution 12.2 g of HgO dissolved in a mixture of 30 ml of glacial AcOH and 30 ml of H_2O was added to a solution of I dissolved in 50 ml of 5% NaOH solution with stirring, the pH was adjusted to 5.0—5.8, and the mixture was refluxed at 130—140° for *ca.* 20 hr. CO_2 evolved during the refluxing was absorbed in the $Ba(OH)_2$ solution and the refluxing was continued until the $Ba(OH)_2$ solution no longer became turbid.

The refluxed solution was filtered while hot, the solid was washed with glacial AcOH and H_2O, dried and washed with MeOH, affording 16 g of III as fine white crystals, mp 300°. *Anal.* Calcd. for $C_8H_8HgO_2$: C, 28.57; H, 2.38. Found: C, 28.77; H, 2.46. Detection of Hg: a) X-ray intensity method: Hitachi model GF–S was used. b) Atomic absorption photometry: Hitachi model 207 was used. The sample was made into 50% AcOH saturated solution.

3-Chloromercuri-2-carboxy-5-norbornene (IV)——A solution of 1.0 g of III dissolved in 20 ml of 2 N NaOH was warmed on a water bath at 70° for 1 hr, cooled, and acidified with HCl.

The white crystals that precipitated out on standing were recrystallized from acetone to give 500 mg of IV, mp 215—217°. *Anal.* Calcd. for $C_8H_9ClHgO_2$: C, 25.77; H, 2.42. Found: C, 26.01; H, 2.57. UV λ_{max}^{MeOH}: 215 nm (log ε 4.669); IR ν_{max}^{KBr}: 1775 cm^{-1} (CO); NMR (in Me_2SO) δ: 4.89—4.84 (1H, d, CH=CH, J= 6.57 Hz); 13.0 (1H, s,b, COOH); Mass Spectrum m/e: 372 (M^+).

3,3′-Dithio-di(2-carboxy-5-norbornene) (V)——H_2S gas was passed through a suspension of 1.0 g of III in a mixture of 20 ml of glacial AcOH and 1.0 ml H_2O, black precipitate of HgS was completed after about 20 min, and then H_2S was passed for further 10 min. The precipitate was filtered, the filtrate was evaporated under a reduced pressure, and the residue was chromatographed over silica gel. The column was eluted with acetone–ether (3: 1) and 100 mg of V, mp 118—121°, was obtained from the eluate. *Anal.* Calcd. for $C_{16}H_{16}O_4S_2$: C, 56.80; H, 5.33; S, 18.93; Found: C, 57.01; H, 5.47; S, 19.08.

3-Cyano-2-carboxy-5-norbornene (VII)——To a suspension of 2.0 g of III in a mixture of 30 ml of glacial AcOH and 2 ml of H_2O, 0.5 g of solid NaCN was added and the mixture was shaken throughly at room tem-

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[4] C. Larock and C. Bernhardt, *J. Org. Chem.*, **42**, 1680 (1977).
[5] C. Larock and A. Felloes, *J. Org. Chem.*, **43**, 131 (1978).

perature, by which the reactants were dissolved completely. After standing for *ca.* 3 hr, the mixture was warmed on a water bath at 50—60° and glacial AcOH was distilled off at a reduced pressure. The residue was extracted with acetone, the solvent was evaporated from the extract, and the residue was dissolved in NaOH solution.

This solution was acidified with HCl and allowed to stand to give 100 mg of VII precipitated out as white columnar crystals, mp 221—224°. *Anal.* Calcd. for $C_9H_9NO_2$: C, 66.25; H, 5.52; N, 8.57. Found: C, 66.54; H, 5.68; N, 8.83. UV λ_{max}^{MeOH}: 220 nm (log ε 4.265); IR ν_{max}^{KBr} cm^{-1}: 1770 (CO), 2330 (CN); NMR (in $CDCl_3$) δ: 9.10 ppm (1H), s, (COOH); Mass Spectrum *m/e*: 163 (M^+).

3-Iodo-2-carboxy-5-norbornene (VIa) and 3-Iodomercuri-2-carboxy-5-norbornene (VIb)——To a suspension of 1.0 g of III in a mixture of 20 ml of glacial AcOH and 1.0 ml of H_2O 1.0 g of KI was added and the mixture was warmed on a water bath 1 hr at 70—80° by which the reactants were dissolved completely. After cooling scarlet HgI_2 precipitate was filtered off, the filtrate was evaporated under a reduced pressure, and the residue was recrystallized from benzene-acetone to give 600 mg of VIb (mp 199—203°).

The mother liquor left after separation of these cystals was purified to afford 100 mg of VIa, mp 102—104°.

VIb: *Anal.* Calcd. for $C_8H_9HgIO_2$: C, 20.73; H, 1.94. Found: C, 20.99; H, 2.20. UV λ_{max}^{MeOH}: 217 nm (log ε 4.363); IR ν_{max}^{KBr}; 1770 cm^{-1} (CO); NMR (in Me_2SO) δ: 13.0 ppm (1H), broad singlet (COOH); Mass Spectrum *m/e*: 463 (M^+).

VIa: *Anal.* Calcd. for $C_8H_9IO_2$: C, 36.50; H, 3.42. Found: C, 36.82; H, 3.66; UV λ_{max}^{MeOH}: 220 nm (log ε 4.131); IR ν_{max}^{KBr}; 1760 cm^{-1} (CO).