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Metal-free phthalocyanine was prepared from *o*-phthalonitrile using the benzenetelluroate ion in ethanol. Furthermore, the yield of metal-free phthalocyanine using the benzenetelluroate ion was compared with that using the benzeneselenolate ion or the benzenethiolate ion.

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Phthalocyanines (Pc) are attracting much attention as a new functional material. Several methods for synthesizing metal-free phthalocyanine (H_2Pc) from *o*-phthalonitrile (Phn) have been reported [1-3]. Tomoda *et al.* investigated the preparation using an alkoxylate ion generated from alcohol and an organic strong base such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) or 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) [4]. We report here the preparation of H_2Pc using the benzenetelluroate ion (**1**) which is more nucleophilic than the alkoxylate ion. Compound **1** was obtained by the reduction of diphenylditelluride (**2**). Recently, the application of tellurium reagents in organic synthesis were investigated [5].

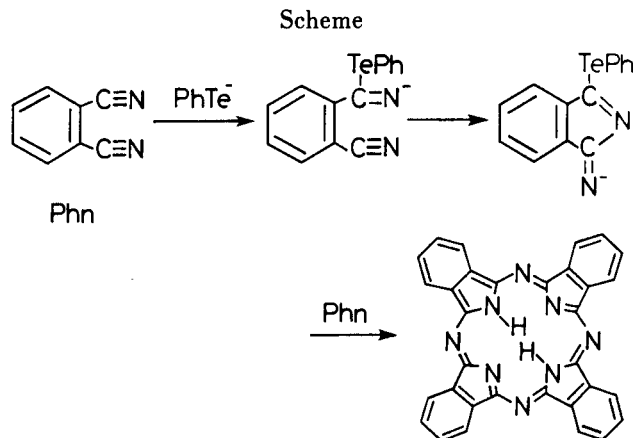
The formation conditions of H_2Pc concerning **2**/Phn molar ratio and the reaction time were examined. These results are summarized in the Table. When **2**/Phn was 0.10, H_2Pc could be obtained in the highest yield of 57% (Table, Entry 2-6). At an equal molar ratio, the yield of

Table

Entry	Molar ratio 2 /Phn	Reaction time hour	Yield %
1	0.01	6	4
2	0.05	6	22
3	0.10	6	57
4	0.20	6	48
5	0.40	6	40
6	1.00	6	trace
7	0.10	4	32
8	0.10	12	50
9	0.10	24	50

Phn 10 mmoles.

H_2Pc was lowered because of the formation of tar. The yield of H_2Pc increased with increasing reaction time but was approximately constant after 6 hours (Table, Entry 3,7-6). This reaction is considered to proceed by a nucleophilic attack of the benzene-telluroate ion at the cyano group of Phn as shown in the Scheme.



The X-ray diffraction pattern of H_2Pc prepared by this method agrees with that prepared by the DBU method. Furthermore, the reaction of Phn with the benzeneselenolate ion and the benzenethiolate ion generated by the reduction of diphenyl diselenide and diphenyl disulfide under the same conditions afforded H_2Pc in yields of 53% and 34%, respectively. The benzeneselenolate ion was effective for the preparation of H_2Pc as well as the benzenetelluroate ion.

Further investigation on the preparation of Pc derivatives and isolation of the intermediates are in progress.

EXPERIMENTAL

The ir, ms and electronic spectrum were recorded by means of a JASCO IRA-2, Shimazu QP-1000 and Shimazu UV-2100, respectively.

Materials.

Diphenyl ditelluride and diphenyl diselenide were prepared by the reaction of phenylmagnesium bromide with tellurium and selenium, respectively [6,7].

Preparation of H_2Pc .

According to reference [8], the benzenetelluroate ion was generated from diphenyl ditelluride (**2**) (1 mmole) with sodium borohydride (2.5 mmoles) in dry ethanol (10 ml) at room temperature under a nitrogen atmosphere. Phn (10 mmoles) in dry ethanol (50 ml) was added and the mixture was refluxed. The precipitate was filtered off, washed with hot ethanol and acetone until the fil-

trate became colorless and dried to give H₂-Pc; ir (potassium bromide): 3280 cm⁻¹ (NH); ms: m/e 514 (M⁺); vis (1-chloronaphthalene): λ max 602 (log ε 4.47), 636 (4.64), 644 (4.63), 664 (5.14), 699 (5.18).

Anal. Calcd. for C₃₂H₁₈N₆: C, 74.69; H, 3.53; N, 21.78. Found: C, 74.92; H, 3.47; N, 21.83.

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