Studies on Meso-ionic Compounds. IX[1)]*. *Sydnone-4-carboxylic acid via Lithium Compound*

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Although a large number of sydnone derivatives have been obtained, attempts to prepare sydnone-4-carboxylic acid (III) have not yet been successful. 3-Phenyl-4-bromosydnone (I) did not react with potassium cyanide[2)], nor did the Grignard reagent derived from the bromo-compound I react with carbon dioxide[3)]. On the other hand, many attempts to prepare III by oxidizing the methyl group of 3-phenyl-4-methylsydnone have not been promising[4)]. After many trials, the authors have finally succeeded in preparing III via lithium compound.

Among many methods proposed for the preparation of organolithium compounds, the authors have tried halogen-metal interconversion method, because it has been known that the ease of interconversion depends on the degree of positive polarization of the halogen atom[5)], and it has been reported that the bromine atom of 4-bromosydnone (I) has the tendency to be removed as positive ion[2)]. In accordance with the above consideration, 3-phenyl-4-bromosydnone (I) reacted smoothly with *n*-butyl-lithium to give the corresponding lithium compound (II), which in turn,

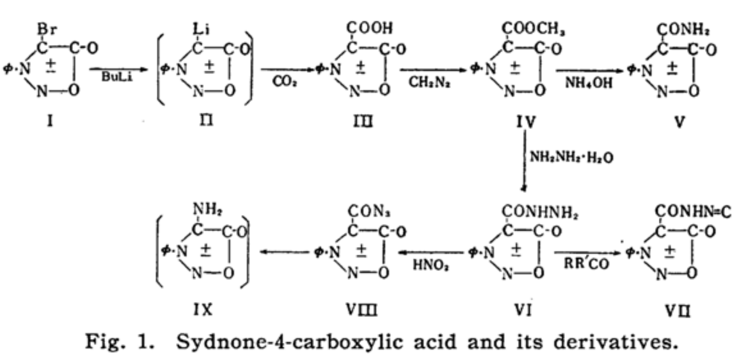

Fig. 1. Sydnone-4-carboxylic acid and its derivatives.

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1) Part VIII. M. Hashimoto and M. Ohta, This Bulletin, **31**, 1048 (1958).

2) H. Kato and M. Ohta, ibid, **30**, 210 (1957).

3) M. Ohta and H. Kato, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **78**, 1653 (1957).

4) Unpublished results of the experiment carried out by M. Hashimoto.

5) R. G. Jones and H. Gilman, *Organic Reactions*, **6**, 339 (1951).

reacted with carbon dioxide to give the expected 3-phenylsydnone-4-carboxylic acid (III). The acid gave the ester IV by reaction with diazomethane, and the ester gave the corresponding amide (V) or hydrazide (VI) by the action of ammonia or hydrazine hydrate, respectively. The hydrazide is rather unstable and is converted, by warming, into an unidentified compound. This compound is negative to Liebermann's nitroso test, but turns positive to it after being warmed with 5% sodium hydroxide solution, which suggests the maintenance of sydnone nucleus in that compound[6].

The hydrazide VI is characterized by its ready formation of hydrazones VII by reaction with ketones (see Table 1). When the hydrazide was treated with sodium nitrite in acetic acid, the corresponding azide VIII was obtained, but the authors succeeded in preparing neither aminosydnone IX nor its derivatives by Curtius or its modified reactions. As a considerable number of attempts to prepare aminosydnone IX by reduction of 4-nitrosydnone have been unsuccessful[4,7], the stability of this supposed compound might be called in question.

Experimental

3-Phenyl-4-bromosydnone (I).—The method of preparation of this compound is a little different from those reported earlier[8]. Into a solution of 50 g. of 3-phenylsydnone and 50 g. of fused sodium acetate in 400 cc. of glacial acetic acid was added dropwise 50 g. of bromine under cooling and stirring. After a few minutes, the solution was diluted with a large quantity of water and the precipitate which separated out was filtered off. Recrystallization from ethanol gave 57 g. of white needles, m.p. 141°C.

3-Phenylsydnone-4-carboxylic acid (III).—A solution of *n*-butyl-lithium in 100 cc. of ether prepared from 3.1 g. of lithium metal and 35 g. of *n*-butyl bromide[9] was added dropwise to a suspension of 35 g. of 3-phenyl-4-bromosydnone in 70 cc. of anhydrous ether under a stream of nitrogen and under stirring and cooling to −50°C. After thirty minutes, the reaction mixture was poured over 50 g. of powdered dry ice. When all the dry ice had been evaporated, the mixture was decomposed with water and the aqueous layer was washed three times with benzene and acidified with hydrochloric acid. The precipitate which separated out was collected and recrystallized from ethanol giving 25 g. of white needles, m.p. 193°C (decomp.).

Anal. Found: C, 52.16; H, 3.19; N, 13.68. Calcd. for $C_9H_6O_4N_2$ (III): C, 52.43; H, 2.93; N, 13.59%.

Methyl 3-phenylsydnone-4-carboxylate (IV).—Diazomethane prepared from 2 g. of *N*-nitroso-*N*-methyl-*p*-toluenesulfonamide was absorbed into a suspension of 0.5 g. of III in 20 cc. of ether. After a few minutes, the solution was concentrated and the crystals which separated out were collected and recrystallized from methanol giving 0.47 g. of colorless leaflets, m.p. 142°C (decomp.)

Anal. Found: N, 12.44. Calcd. for $C_{10}H_8O_4N_2$ (IV): N, 12.72%.

3-Phenylsydnone-4-carboxamide (V).—In 5 cc. of concentrated aqueous ammonia was suspended 0.2 g. of III. After being kept standing for three days under room temperature, the precipitate was collected and recrystallized from ethanol giving 0.13 g. of colorless needles, m.p. 227°C (decomp.).

Anal. Found: N, 20.50. Calcd. for $C_9H_7O_3N_3$ (V): N, 20.48%.

3-Phenylsydnone-4-carboxylic acid hydrazide (VI).—Into a solution of 10 cc. of hydrazine hydrate and 4 cc. of methanol was added 10 g. of IV. After three hours, the crystals which separated out were collected, dissolved in chloroform, and reprecipitated by addition of ligroin, giving 9 g. of yellow needles. This compound was turned into a dark red substance by warming; the latter decomposed at 303°C.

Anal. Found: C, 49.05; H, 3.99; N, 25.07. Calcd. for $C_9H_8O_3N_4$ (VI): C, 49.09; H, 3.66; N, 25.45%.

When VI was warmed in methanol or in xylene, a dark red substance of m.p. 303°C (decomp.) separated out, which is insoluble in most solvents.

Anal. Found: C, 45.92; H, 3.12; N, 25.36%.

This compound was negative to Liebermann's nitroso test, but turned positive to it after warming two hours with 5% sodium hydroxide solution.

When VI was treated with carbonyl compounds at room temperature, the corresponding hydrazones VII were obtained. Some of the derivatives of this type are listed in Table I.

Example: To 0.1 g. of VI was added a few drops of acetone. After a few minutes, petroleum ether was added and the crystals which separated out were collected, dissolved in acetone and reprecipitated by addition of petroleum ether giving 0.08 g. of white fine needles, m.p. 144~146°C (decomp.).

3-Phenylsydnone-4-carboxylic acid azide (VIII).—Into a solution of 0.6 g. of VI in 10 cc. of 50% aqueous acid, was added 0.2 g. of sodium nitrite under cooling. After thirty minutes, water was added and the crystals which separated out were collected, dissolved in acetic acid and reprecipitated by addition of water affording 0.52 g. of white needles, m.p. 102°C (decomp.).

Anal. Found: C, 46.78; H, 2.54; N, 30.37. Calcd. for $C_9H_5O_3N_5$ (VIII): C, 46.75; H, 2.18; N, 30.30%.

When VIII was heated in ethanol, water or a

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[6] J. C. Earl and A. W. Mackney, *J. Chem. Soc.*, **1935**, 899.

[7] W. Baker, W. D. Oillis and V. D. Poole, ibid., **1950**, 1542.

[8] H. Kato and M. Ohta, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **77**, 1304 (1956).

[9] R. G. Jones and H. Gilman, *Organic Reactions*, **6**, 352 (1951).

TABLE I

HYDRAZONES (VII) DERIVED FROM 3-PHENYLSYDNONE-4-CARBOHYDRAZIDE (VI) AND CARBONYL COMPOUNDS

carbonyl compd.	m.p. (°C)*	characteristics	formula	N found	N calcd.
acetone	144∼146	white needle[a)]	$C_{12}H_{12}O_3N_4$	21.59	21.53
methyl ethyl ketone	147	white needle[b)]	$C_{13}H_{14}O_3N_4$	20.50	20.43
benzaldehyde	219	pale yellow amorph.[c)]	$C_{16}H_{12}O_3N_4$	18.13	18.18
cyclohexanone	130	white amorph.[b)]	$C_{15}H_{16}O_3N_4$	17.93	18.66
acetophenone	224	pale yellow amorph.[c)]	$C_{17}H_{14}O_3N_4$	17.22	17.38

* All melting points are with decomposition.

Recrystallized from: a) acetone—petroleum ether; b) benzene—ligroin; c) benzene.

solution of phthalic anhydride in pyridine, no identifiable substance could be isolated. When VIII was heated in acetic anhydride for fifteen minutes on a water bath, the solvent was removed under reduced pressure, and the residue treated with water, a solid substance was obtained, which soon underwent decomposition with evolution of gas giving an unidentified oily substance.

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