Studies on Meso-ionic Compounds. III[1]. *Reactions of 3-Phenyl-4-bromosydnone*

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In the first paper of this series[1], the conditions for preparing 3-phenyl-4-bromosydnone (I) from 3-phenylsydnone (II) have been reported in detail, and it has been shown that an excellent result was obtained by treating an ether suspension of II with bromine in the presence of sodium bicarbonate, or by refluxing a chloroform solution of II with N-bromosuccinimide, but an attempt to prepare I by the method described by Baker et al.[2] was unsuccessful. The present investigation was undertaken to study the reactions of I, since previous communications[3] on sydnones have dealt almost exclusively with their unusual structure, and little attention has been paid to their reactions.

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[1] Part I, II. H. Kato, K. Nakahara and M. Ohta, *J. Chem. Soc. Japan* (*Pure Chem. Sect.*), **77**, 1304 (1956).

[2] W. Baker, W D Ollis and V. D. Poole, *J. Chem. Soc.*, **1949**, 307

[3] Works on this subject are reviewed by M. Ohta in *Chemistry and Chemical Industry Japan*, **9**, 311 (1956).

For instance, what are reported so far about I, are only its methods of preparation[1,2,4] and its decomposition reactions[4,5] by the action of acid or alkali.

When I was treated with sodium salt of *p*-thiocresol, it did not afford the expected 4-*p*-tolyl sulfide of II, but I was reduced to II and *p*-thiocresol was oxidized to form di-*p*-tolyl disulfide (III). The reaction of I with sodium hydrosulfide was then tried, and this procedure gave, quite unexpectedly, II and sulfur as reaction products. The same reaction products were obtained when I was treated with sodium sulfide. Considering the above reactions, it seems reasonable to conclude that I has a marked oxidative property. This consideration is further supported by the observation that iodine was liberated when an ethanolic solution of I and potassium iodide was kept standing at room temperature in the presence of diluted hydrogen chloride.

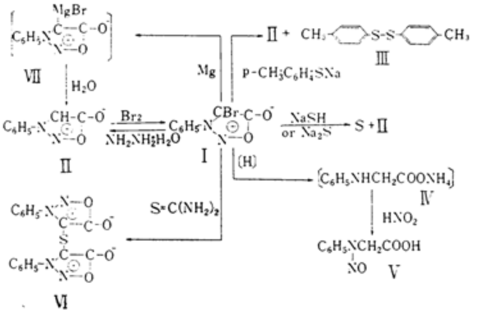
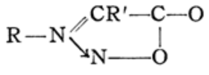
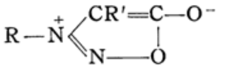


Fig. Reactions of 3-Phenyl-4-bromosydnone.

When warmed with an exess amount of hydrazine hydrate, I was reduced to II, but when an equimolecular amount of hydrazine hydrate in ethanol was used, I was recovered unchanged even after refluxing for prolonged hours. An attempt to remove the bromine atom by the action of diethylamine and Raney nickel was unsuccessful. When I was subjected to reduction with zinc dust in aqueous acetic acid, the bromine atom was removed but was accompanied by a reductive fission of the sydnone ring at the N–N bond, thus affording the ammonium salt of N-phenylglycine (IV), which was identified by conversion to N-nitroso-N-phenylglycine (V). It was not possible to determine which one of the two reactions, viz. the removal of the bromine atom or the cleavage of the sydnone ring, precedes the other. This mode of ring cleavage at the N–N bond is in accord with that reported by Earl[6] in the case of II. Considering this mode of ring cleavage, Earl concluded that, of the structures VIII and IX formerly proposed for the sydnones[7], structure VIII is more favoured. But the fact that II is considerably soluble in highly polarized solvent e. g., chloroform, acetic acid or pyridine, and only sparingly soluble in carbon tetrachloride, benzine or ether favors rather the betaine type structure IX.


VIII


IX

It seems inappropriate to conclude from these data alone reported by Earl, which structure of the two should be more favoured. Moreover, now that the structures of sydnones are best explained by molecular orbital theory[8], a trial to show their structures by conventional covalent formulae seems to have little significance.

When I was treated with thiourea, pale yellow needles (VI) melting at 164—165°C. were obtained. This substance was proved to contain sulfur, and had an empirical formula of $C_{16}H_{10}O_4N_4S$ and was insoluble in 10% sodium hydroxide solution and 10% hydrochloric acid. Woodbridge et al.[9] have reported that the reactions of 4-substituted-2-aminothiazoles with thiourea and iodine or bromine give di-5-thiazolyl sulfides. Considering the properties of VI and the above reactions on thiazoles it is evident that I reacted with thiourea to afford 4-bis (3-phenylsydnonyl) sulfide (VI) by an analogous reaction, though the mechanism of this is not known.

As for the reaction of I with magnesium metal, I did not react even at an elevated temperature when magnesium alone was used, but on adding methyl iodide I began to react smoothly with magnesium metal and went into solution. On decomposing the reaction product with water, II was obtained. From this fact, it is evident that in the presence of methyl iodide, I is capable of forming the corresponding Grignard reagent (VII).

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[4] J. Kenner and K. Mackay, *Nature*. **158**, 909 (1946).

[5] R. A. Eade and J. C. Earl, *J. Chem. Soc.*, **1948**, 2307.

[6] J. C. Earl, *Rec. trav. chim. Pay-Bas*, **75**, 346(1956).

[7] J. C. Earl, *Chemistry and Industry*, **1953**, 746, W. Baker and W. D. Ollis, *Nature*, **158**, 703 (1936).

[8] H. C. Longuet-Higgins, *J. chim. phys.*, **46**, 244 (1949) ; L. E. Orgel, T. L. Cottrel, W. Dick and L. E. Sutton, *Trans. Faraday Soc.*, **47**, 113 (1951).

[9] R. G. Woodbridge and G. Dougherty, *J. Am. Chem. Soc.*, **71**, 1744 (1949).

No reaction occurred except a partial decomposition when I was treated with silver nitrate, sodium nitrite, sodium phenolate, acetyl nitrate, guanidine or sodium iodide.

In conclusion, the sydnone ring is highly aromatic in character, and I is inert to usual anionoid reagents. Most reactions reported here can be interpreted only when the oxidative effect of I is taken into consideration. Further studies on the reactions of I and VII are now under experiment.

Experimental

3-Phenyl-4-bromosydnone (I).—Into a suspension of lg. of II and 2g. of sodium bicarbonate in 30 cc. of ether was added lg. of bromine under stirring. After a few minutes, the reaction mixture was filtered and washed with water, and was recrystallized from ethanol giving 1.15 g. (yield 78%) of white needles, m. p. 141°C. (decomp.). Baker et al.[2] reports its m. p. 140°C. (decomp.). I turns to a red color on prolonged exposure to sunlight.

Reaction of I with *p*-Thiocresol.—To a solution of 0.5 g. of *p*-thiocresol in 20 cc. of anhydrous methanol containing 0.1 g. of metallic sodium was added lg. of I under stirring at room temperature. After standing overnight, the solvent was evaporated under reduced pressure and the residue was first washed with water and then extracted with ether. The ether extract was evaporated to dryness and the residue was crystallized from methanol giving 0.4 g. of colorless leaflets, m. p. 47—48°C.. The melting point of this substance was not depressed by admixture with authentic di-*p*-tolyl disulfide. The residue (0.4 g.) left after the extraction with ether was recrystallized twice from ethanol giving 0.15 g. of white needles melting at 134—135°C. with slight decomposition, undepressed by admixture with authentic II.

Reaction of I with Sodium Hydrosulfide.—A solution of 0.09 g. of sodium hydroxide in 15cc. of methanol was saturated with dry hydrogen sulfide gas. To this solution were added 0.5 g. of I and a small amount of potassium iodide, both of which soon went into solution and pale yellow precipitate began to separate out. Stirring was continued for three hours at room temperature and then allowed to stand overnight. The pale yellow precipitate which separated out was filtered and was extracted with a small amount of carbon disulfide. On evaporating the carbon disulfide 0.1 g. of pale yellow amorphous powder (m. p. 120°C.) was obtained, which was identified as sulfur. The filtrate was evaporated under reduced pressure and the orange colored residue was washed with water and recrystallized from ethanol giving 0.23 g. of slightly brown colored long needles, m. p. 133—134°C. with slight decomposition, undepressed by admixture with authentic II.

Reaction of I with Sodium Sulfide.—To a methanol solution (15 cc.) of sodium hydrosulfide, prepared from 0.09 g. of sodium hydroxide by the same way as is described above, was added 0.09 g. of sodium hydroxide. One gram of I was added to this solution and was treated by essentially the same method as in the preceeding experiment. This also gave II and sulfur, both of which were identified by their melting points and mixed melting points with authentic samples.

Hydrogenolysis of I with Zinc Dust.—Into a solution of 0.5 g. of I in 20 cc. of 80% aqueous acetic acid was added portionwise 2 g. of zinc dust during two hours under stirring and cooling by water. Stirring was continued for six hours and allowed to stand overnight. This was filtered and the residue was washed with water. This filtrate was negative to Liebermann's nitroso test. A part (1/5) of this filtrate was made alkaline with sodium hydroxide, which evolved ammonia on heating. The residue was decomposed by hydrochloric acid and was added to the other part (4/5) of the filtrate. This solution was concentrated to 10 cc. under reduced pressure and the remaining acetic acid was extracted with ether. After evaporating the ether which was dissolved in water under reduced pressure, this solution was acidified with hydrogen chloride. To this solution was added dropwise a solution of 0.15 g. of sodium nitrite under stirring and ice cooling. The pale yellow precipitate (0.16 g.) which separated out was dissolved in 5% sodium bicarbonate solution, which on acidification with hydrogen chloride afforded pale yellow needles, m. p. 101—102°C. (decomp.). This substance was negative to Beilstein's halogen test and gave a strong Liebermann's nitroso test. A mixed m. p. with authentic N-nitroso-N-phenylglycine was 102—103°C. (decomp.).

Reaction of I with Thiourea.—To 20 cc. of ethanol were added 1 g. each of I and thiourea and was refluxed for six hours. After standing overnight, the pale yellow needles which separated out were collected by filtration (0.2 g. m. p. 157°C.), and recrystallized first from acetone and then from ethanol giving pale yellow needles, m. p. 164—165°C.. This substance was negative to Beilstein's halogen test, insoluble in 10% sodium hydroxide solution and in 10% hydrochloric acid, and gave a positive sulfur test.

Anal. Found: C, 54.47; H, 3.22; N, 15.83. Calcd. for $C_{16}H_{10}O_4N_4S$: C, 54.24; H, 2.85; N, 15.81%.

The same result was obtained when an equimolecular amount of thiourea was used, but the yield in this case was poorer and a considerable amount of I was recovered unchanged, accompanied by a small amount of sulfur.

Reaction of I with Magnesium Metal.—To a suspension of 0.5 g. of I and 0.22 g. of magnesium ribbons in 10 cc. of anhydrous ether, was added 1.0 g. of methyl iodide under stirring. After three hours the reaction was nearly completed. Water was added and was evaporated to dryness under reduced pressure, and the residue was extracted with ethanol. On evaporating the solvent under reduced pressure, a small amount of oily substance was obtained, which became solidified on adding water; recrystallization of this substance (0.17 g.) from ethanol gave 0.1 g. of white needles, m. p. 134—135°C. with slight decomposition. The melting point of this substance was not depressed by admixture with authentic II. In the absence of methyl iodide, no reaction occurred even when *n*-butyl ether was used as the solvent and the reaction was conducted at 100°C..

Reaction of I with Hydrazine Hydrate.—To 1 cc. of 80% hydrazine hydrate were added 0.5 g. of I and a few drops of ethanol and this mixture was gently refluxed on a water bath for four hours, and was kept standing overnight. On adding water, 0.1 g. of pale brown needles melting at 132—135°C. were separated out, recrystallization of which from dilute ethanol gave pale yellow needles, m. p. 134°C. with slight decomposition. A mixed m. p. with authentic II was 135°C.. When I was refluxed in ethanol with equimolecular amount of hydrazine hydrate, no reaction occurred and I was recovered unchanged.

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