Studies on Meso-ionic Compounds. VIII[1]. *Oxidation of Sydnones*

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(Received June 3, 1958)

Substitution reactions of 3-phenylsydnone and the behavior of 3-phenyl-4-bromosydnone suggest us that the sydnone nucleus is aromatic in character to a considerable extent. As many instances are known where a methyl substituent in aromatic heterocycles is oxidized to a carboxylic group, it seemed possible to oxidize 4-methylsydnones to corresponding 4-carboxylic acid derivatives. Although this was not realized, we found an interesting rearrangement during the oxidation of several sydnones.

The oxidation of 3-phenyl-4-methlsydnone (Ia) with potassium permanganate in acetone did not afford the expected carboxylic acid, but the oxidative cleavage of sydnone ring occurred, affording acetophenone. The same reaction product was also obtained by oxidation of Ia with potassium permanganate in aqueous pyridine or with aqueous hydrogen peroxide in acetic acid. In each case a slight evolution of gas was observed. The results obtained here suggest that the rearrangement of a phenyl group in 3-position of 3-phenyl-4-methylsydnone from nitrogen (3-position) to carbon (4-position) occurred in the course of the oxidation process.

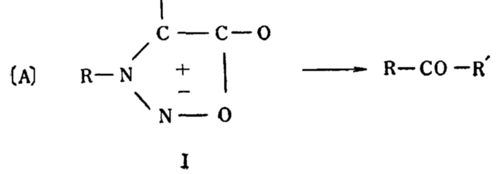

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Fig. 1.

a; $R=C_6H_5$, $R'=CH_3$

b: $R=C_6H_5$, $R'=H$

c: $R=p\text{-}CH_3\cdot C_6H_4$, $R'=H$

d: $R=R'=C_6H_5$

e: $R=o\text{-}CH_3\cdot C_6H_4$, $R'=H$

A reaction of the same type also occurred when 3-phenylsydnone (Ib) and 3-*p*-tolylsydnone (Ic) were treated with aqueous hydrogen peroxide in acetic acid at room temperature, affording benzaldehyde and *p*-tolualdehyde, respectively.

When the same procedure was applied to 3,4-diphenylsydnone (Id) and 3-*o*-tolylsydnone (Ie), however, the expected ketone or aldehyde was not obtained, but the starting materials were recovered unchanged. When 3, 4-diphenylsydnone was heated with a mixture of hydrogen peroxide and acetic acid, a very small amount of phenol was obtained, which was identified by Liebermann's nitroso test, coloration on addition of ferric chloride and formation of tribromophenol.

The oxidation of 3-phenylsydnone (IIa) with potassium permanganate in acetone gave, quite unexpectedly, 3, 4-diphenylsydnone (IIIa) and benzaldehyde. The 3, 4-diphenylsydnone obtained here was identical with a specimen prepared by the method reported by Baker et al.[2]. The oxidation of 3-*p*-tolylsydnone (IIb)

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[1] Part VII of this series, H. Kato and M. Ohta, *J. Chem. Soc. Japan, Pure Chem. Sec.*, (*Nippon Kagaku Zassi*), **78**, 1653 (1957).

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

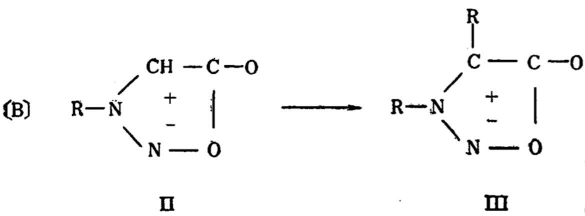

Fig. 2.

a: $R=C_6H_5(=Ib)$ a: $R=C_6H_5(=Id)$
b: $R=p\text{-}CH_3\cdot C_6H_4(=Ic)$ b: $R=p\text{-}CH_3\cdot C_6H_4$

with potassium permanganate also gave 3,4-di-*p*-tolylsydnone (IIIb).

The results obtained above are not quite sufficient for a deduction concerning the reaction mechanism. However, from a consideration of the result obtained in the case of 3-phenyl-4-methylsydnone, it might be assumed that only 3-arylsydnone which has no substituent in 4-position could give 3, 4-diarylsydnone by the action of potassium permanganate, and that 4-substituted sydnone was oxidized to ketone. On the basis of this fact, it seems reasonable to conclude that the intermolecular rearrangement described above was preceded by the formation of aryl radical by the action of potassium permanganate on sydnone, followed by the attack of the aryl radical on 4-position of the unchanged sydnone. The value of the free valence in 4-position of sydnone lends some support to this consideration; namely, according to Orgel et al.[3], a value of 0.562 is calculated, which corresponds with that of free valence in 9- or 10-position of anthracene where radical substitution occurs readily. For the determination of the mechanism of such reactions, however, a more detailed investigation will probably be required.

Two novel types of the rearrangement reaction presented in this paper, have not yet been observed with heterocyclic compounds.

Experimental

Oxidation of 3-Phenyl-4-methylsydnone (Ia) with Potassium Permanganate.—a) To a solution of 4.4 g. of Ia, prepared by Earl's method[4], in 200 cc. of acetone was added portionwise 7.9 g. of finely powdered potassium permanganate with stirring at room temperature. After being kept overnight, the precipitated manganese dioxide was filtered off and the filtrate was evaporated. From the residue was obtained an oily product boiling at 68°/17 mm., 2,4-dinitrophenylhydrazone of which melted at 239~240°, and did not show any melting point depression on admixture with the authentic 2, 4-dinitrophenylhydrazone of acetophenone (m. p. 238°).

b) In aqueous pyridine, 4.4 g. of Ia was oxidized with 7.9 g. of potassium permanganate at room temperature. After being kept overnight, the precipitated manganese dioxide was filtered off and the filtrate was evaporated under reduced pressure. The residue was extracted with ethanol and the ethanol was removed. The crude reddish brown oil, dissolved in benzene and passed through an alumina column, gave 0.34 g. of Ia and an oily product, 2,4-dinitrophenylhydrazone of which did not show any melting point depression on admixture with the authentic 2,4-dinitrophenylhydrazone of acetophenone.

Oxidation of Ia with Hydrogen Peroxide.—To a solution of 8.8 g. of Ia in 20 cc. of glacial acetic acid was added 8.4 g. of aqueous 30% hydrogen peroxide and this was kept standing at room temperature for 29 hours. The reaction mixture was diluted with 80 cc. of water, neutralized by sodium carbonate and extracted with ether. The extracts were washed with aqueous sodium bicarbonate and dried. An oily product (1.3 g.) gave phenylhydrazone (m. p. 101°) and 2, 4-dinitrophenylhydrazone (m. p. 239°) which did not show any melting point depression on admixture with those of acetophenone, respectively.

Oxidation of 3-Phenylsydnone (Ib) with Hydrogen Peroxide.—a) To a solution of 4 g. of Ib, prepared by our method[5], in 25 cc. of glacial acetic acid was added 4.2 g. of aqueous 30% hydrogen peroxide. After standing at room temperture for 24 hours, the reaction mixture was treated by the same procedure as described above. An oily product obtained gave phenylhydrazone (m. p. 155~156°) and 2, 4-dinitrophenylhydrazone (m. p. 233°), both of which showed no melting point depression on admixture with the authentic samples obtained from benzaldehyde.

b) When Ib was treated by the same procedure as described in a) except that the reaction time was 5 hours, 70% of Ib was recovered.

Oxidation of 3-*p*-Tolylsydnone (Ic) with Hydrogen Peroxide.—When a mixture of Ic, prepared by Baker's method[2], and 20 cc. of glacial acetic acid and 2.1 g. of aqueous 30% hydrogen peroxide was kept standing at room temperature for 24 hours, and then treated by essentially the same method as described above, *p*-tolualdehyde was obtained and identified as phenylhydrazone (m. p. 112°) and 2, 4-dinitrophenylhydrazone (m. p. 230°).

3-*o*-Tolylsydone (Ie).—A suspension of 29 g. of *o*-tolylglycine, prepared by Steppes' method[6], in 350 cc. of water was treated with 20 cc. of concentrated hydrochloric acid and cooled at 0°. A solution of 13 g. of sodium nitrite in 35 cc. of

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[3] L. E. Orgel, T. L. Cottrell, W. Dick and L. E. Sutton, *Trans. Faraday Soc.*, **47**, 113 (1951).

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

[5] M. Hashimoto and M. Ohta, *J. Chem. Soc. Japan, Pure Chem. Sec.*, (*Nippon Kagaku Zassi*), **78**, 181 (1957).

[6] F. Steppes, *J. prakt. Chem.*, [2] **62**, 491 (1900).

water was added dropwise with vigorous stirring. After an hour dark brown viscous oil had separated. The oil was dissolved in ether, washed with water and dried and the ether was evaporated. Reddish brown oil was obtained, giving a positive Liebermann's nitroso test. Yield 37.2 g. In 200 cc. of acetic anhydride was dissolved 37.2 g. of the crude nitroso acid, kept standing for three days at room temperature, and water was then added. The solid which separated out was collected and washed with aqueous sodium carbonate and water. White flakes were obtained, m. p. 86°, yield 6.8 g.. An analytical sample was prepared by recrystallization from water, m. p. 96° (the reported melting point[7] is 89°). *Anal.* Found: N, 15.66. Calcd. for $C_9H_8O_2N_2$: N, 15.90%.

Reaction of 3-*o*-Tolylsydnone (Ie) with Hydrogen Peroxide.—A mixture of 1.1 g. of Ie and 20 cc. of glacial acetic acid and 1.05 g. of aqueous 30% hydrogen peroxide was kept standing at room temperature for 24 hours, and then diluted with water. White crystals separated out (m. p. 96°, 0.57 g.), undepressed on admixture with Ie.

When the filtrate was neutralized with sodium carbonate, and extracted with ether and the ether was evaporated, 0.16 g. of Ie was still recovered.

Reaction of 3,4-Diphenylsydnone (Id) with Hydrogen Peroxide.—When a mixture of 24 g. of Id and 20 cc. of glacial acetic acid and 1.7 g. of aqueous 30% hydrogen peroxide was treated with the same procedure as described above, 2.22 g. of Id was recovered.

b) A mixture of 2.4 g. of Id and 20 cc. of glacial acetic acid and 1.7 g. of aqueous 30% hydrogen peroxide was heated for 5 hours at 90°, and diluted with 100 cc. of water. The crystals which separated out were recrystallized from ethanol, m. p. 181∼181.5°, undepressed by admixture with Id. Yield 0.61 g..

The acidic filtrate was neutralized with sodium bicarbonate, and extracted with ether and then the ether was evaporated. A very small amount of oil with a smell of phenol was obtained, giving a positive Liebermann's nitroso test and a red ferric chloride reaction, and afforded a bromoderivative which showed no melting point depression on admixture with the authentic sample of tribromophenol.

Oxidation of 3-Phenylsydnone (IIa) with Potassium Permanganate.—To a solution of 8.1 g. of IIa in 400 cc. of acetone was added portionwise 15.8 g. of finely powdered potassium permanganate with stirring at room temperature. After being kept overnight, the precipitated manganese dioxide was filtered off and the acetone was removed. From the residue light yellow crystals separated out, and were collected and recrystallized from ethanol. Pale yellow prisms, m. p. 183∼184.5°, were obtained and did not show any melting point depression on admixture with 3,4-diphenylsydnone (IIIa), prepared by Baker's method[2]. Yield 1.1 g., 22%.

The filtrate (2.1 g.) gave 2,4-dinitrophenylhydrazone, m. p. 233°, undepressed on admixture with the authentic 2,4-dinitrophenylhydrazone of benzaldehyde.

Oxidation of 3-*p*-Tolylsydnone (IIb) with Potassium Permangante.—To a solution of 5.28 g. of IIb in 240 cc. of acetone was added 9.48 g. of finely powdered potassium permanganate. The reaction mixture was treated by essentially the same method as described above, and the yellow crystals obtained were recrystallized from ethanol. Light yellow flakes, m. p. 156.5∼157° (the reported melting point[8] for 3,4-di-*p*-tolylsydnone (IIIb) is 156∼157.5°). Yield 0.82 g., 20.6%. *Anal.* Found: N 11.01. Calcd. for $C_{16}H_{14}O_2N_2$: N, 10.52%.

The authors are grateful to Mr. Asaji Kondo for carrying out the microanalyses.

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[7] J. Hadáček et al., *Publs. fac. sci. univ. Masaryk Čišlo*, **357**, 257 (1954).

[8] W. Baker, W. D. Ollis and V. D. Poole, *J. Chem. Soc.*, **1950**, 1542.