SYNTHESIS OF SYDNOQUINOXALINES AND BIS(SYDNONYLPHENYL)UREA

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Abstract—Sydno[3,4-α]quinoxalin-4-one (2) and -4-thione (3) were prepared directly from 3-(o-aminophenyl)sydnone (1) with phenyl isocyanate, 1,1'-carbonyl diimidazol (Colm₂) and phenyl isothiocyanate respectively in good yield. N,N'-Bis[o-(3-sydnonyl)phenyl]urea (4) was also obtained under slightly different conditions between 1 and Colm₂.

INTRODUCTION

Sydnones have been the most extensively studied heterocyclic mesoionic system. However, prior to the review by Ohta and Kata in 1969, no fused sydnones have been reported. Fused sydnones have been synthesized from the o-aminophenylsydnone (1) by treatment with some appropriate reagents. These can be seen in the synthesis of sydno[3,4-α]quinoxalin-4-one, sydno[3,4-α]quinaxaline, and [1,2,3]oxadiazolo[3,4-α][1,2,4]-benzotriazinium-3-olate.

RESULTS AND DISCUSSION

The synthesis of fused sydnones in this report was based upon the addition of an electrophilic centre to the amino nitrogen atom of o-aminophenylsydnone (1). The adduct may then react with the C₄ atom of the sydnone ring to give the desired product. In this regard, phenyl isocyanate, Colm₂ and phenyl isothiocyanate were chosen in consideration of the reactivity with amino group and the commercial availability of these reagents, since resulting intermediates formed were anticipated to be converted into 2 or 3 by the subsequent cyclization.
Reaction of 1 with phenyl isocyanate yielded 2 via an intermediate, \( N\-[o-(3\text{-sydnonyl})\text{phenyl}]-N\'-\text{phenylurea} \) (5). In the analogous reaction with phenyl isothiocyanate, attempts were failed to isolate the thio-intermediate. The product (2) obtained, was identified by comparing with an authentic sample prepared by the method of Coburn and O'Donnell.\(^2\) The reactions of 1 with CoIm\(_2\) yielded 2 and \( N,N\'-\text{bis}[o-(3\text{-sydnonyl})\text{phenyl}]\text{urea} \) (4). An isocyanate intermediate (6) would react with 1 to afford 4 and intramolecular cyclization of 6 gave 2.

The consistency of the main product (4) and by-product (2) in different runs of the reaction of 1 with various excess amount of CoIm\(_2\) heating in toluene has suggested that the formation of 2 was much less in favor than the reaction of 1 with 6. However, over 90% yield of 2 has been achieved by adding the solution of 1 dropwise into a hot solution of CoIm\(_2\). Decomposition of 4 occurred at 210 °C to give 2 and 2-quinolaxinone (7). The latter was also found to be the main product in pyrolysis of 1. The structure of 7 was confirmed by its melting point (mp 271 °C; lit., 271 °C) and uv spectrum reported\(^5\) as well as the spectral data.
**EXPERIMENTAL**

*N-[o-(3-Sydnoneyl)phenyl]-N'-phenylurea (5)*

A mixture of 3-(o-aminophenyl)sydnone (1) (0.5 g, 0.0028 mol) and phenyl isocyanate (0.35 ml, 0.0032 mol) in dry benzene (10 ml) was refluxed for 2 h and then cooled to precipitate colourless amorphous solid, which was washed with ether (10 ml). Recrystallization from ethanol yielded colourless powders of 5 (0.65 g, 74%), mp 178-179 °C; ir 3640, 3140w, 1745s, 1705s, 1600m, 1540m, 1530m, 1520w, 1445m, 1350w, 1320w, 1265w, 1245m, 1205m, 1165m, 940w, 860w, 755m, 730w, 720w cm⁻¹; ¹H nmr (DMSO-d₆, 60 MHz) δ 9.40(s, 1H), 7.00-8.43(m, 11H); Anal. Calcd for C₁₅H₁₂N₄O₃: C, 53.08; H, 2.41; N, 20.53; ms (m/z 296). Found: C, 52.89; H, 2.27; N, 20.51; ms (m/z 296).

**Sydno[3,4-α]quinoxalin-4-one (2)**

(a). Compound (5) (0.5 g, 0.00246 mol) was refluxed in toluene (10 ml) for 4 h in the presence of pyridine (1 ml). After cooling, the contents were filtered and the residue was washed with ether (10 ml) to yield a colourless amorphous powders (0.2 g). Colourless white solid of 2 was obtained in 0.17 g (50%), after recrystallization from ethanol, mp 305 °C (decomp.)(lit.,² mp 306 °C decomp.): which was also confirmed by comparing the ir with that of an authentic sample.²

(b). A solution of 3-(o-aminophenyl)sydnone (1) (0.5 g, 0.0028 mol) in dry toluene (25 ml) was added dropwise, over a period of 1 h, into a hot solution of 1,1'-carbonyldiimidazol (0.6 g, 0.0037 mol) in dry toluene (10 ml) at 100 °C. After cooling and filtering, a colourless solid was obtained, which was recrystallized from ethanol to give 2 (0.52 g) in 91.5% yield.

**Sydno[3,4-α]quinoxalin-4-thione (3)**

A mixture of 3-(o-aminophenyl)sydnone (1) (1.0 g, 0.0057 mol), phenyl isothiocyanate (1.5 ml, 0.0113 mol) and pyridine (0.5 ml) in dry benzene (10 ml) was refluxed for 4 h with stirring and then cooled. The resulting solid was collected and washed with ether (10 ml) to yield a yellow amorphous solid (0.6 g). The crude
product was recrystallised from ethanol to give light orange needles of 3 (0.56 g, 47%), mp 254 °C (decomp.); ir (nujol) 3210w, 3180w, 3120w, 1750s, 1600m, 1530m, 1430m, 1360m, 1280m, 1250w, 1180w, 1140w, 1120m, 1020m, 890w, 845w, 740w, 720w cm⁻¹; ¹H nmr (DMSO-d₆, 60 MHz) δ 7.1-8.2(m); Anal. Calcd for C₉H₅N₃O₲S: C, 49.31; H, 2.28; N, 19.18; ms (m/z 219). Found: C, 49.45; H, 2.21; N, 19.46; ms (m/z 219).

**NN-Bis[o-(3-sydnone)phenyl]urea (4)**

A mixture of 3-(o-aminophenyl)sydnone (1) (0.5 g, 0.0028 mol) and 1,1'-carbonyldiimidazol (0.5 g, 0.008 mol) in dry toluene (15 ml) was heated for 1 h at 100 °C. The content was cooled and filtered. Colourless precipitate obtained was crystallized from DMSO/EtOH mixture to give colourless powders of 4 (0.43 g, 80%), mp 210 °C (decomp.); ir (nujol) 3345w, 3140w, 1756s, 1731m, 1710s, 1607s, 1550m, 1362m, 1257w, 1216w, 1161w, 1079w, 939m, 845w, 752m, 732m cm⁻¹; ¹H nmr (DMSO-d₆, 90 MHz) δ 8.82(b)(disappeared after D₂O exchange), 8.07-7.36(m); ¹³C nmr (DMSO-d₆) 172.89(s), 165.48(s), 136.97(s), 136.81(d), 130.52(d), 128.95(d), 128.8(d), 102.62(d); Anal. Calcd for C₁₇H₁₂N₆O₫: C, 53.68; H, 3.18; N, 22.09; ms (FAB) (m/z+1 381). Found: C, 53.53; H, 3.04; N, 22.35; ms (m/z+1 381).

**Pyrolysis of NN-Bis[o-(3-sydnone)phenyl]urea (4)**

NN-Bis[o-(3-sydnone)phenyl]urea (0.1 g, 0.00026 mol) was placed in a test tube fitted with a cold finger. The content was heated to 210 °C for 20 min, greenish crystals collected from the the wall of the test tube and the cold finger were identified as 2-quinoxalinone (7) (0.009 g, 24%) (all spectral data matched with those reported; mp 271°C; lit., mp 271°C). The residue was triturated in small amount of ether and the solid obtained was then crystallized from ethanol to give colourless solid of sydno[3,4-a]quinoxalin-4-one (2) (0.023 g, 42%).

**REFERENCES**


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