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Mono *S*-Acylated 1,8-Naphthalenedithiol. Isolation and Characterization of Tetrahedral Intermediate in the Intramolecular Acyl Transfer Reaction

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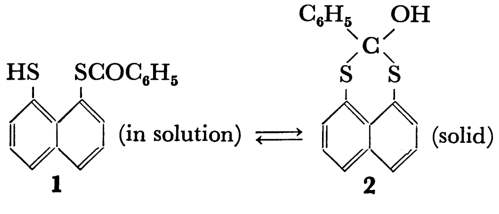
Synopsis. The tetrahedral intermediate in the intramolecular acyl transfer reaction of mono-*S*-acylated 1,8-naphthalenedithiol was found to be sufficiently stable to allow isolation or direct characterization by spectroscopy. Formation of carbenium ion from the intermediate is suggested in sulfuric acid.

Mono-*S*-benzoylation of 1,8-naphthalenedithiol with benzoyl chloride in pyridine under nitrogen afforded the compound with correct data of elemental analysis after purification by column chromatography on silica gel or by simple recrystallization (60—75% yield as monobenzoate). Its IR spectra (Nujol mull), however, show a strong ν_{O-H} band around 3300 cm^{-1} but no absorption for $\nu_{C=O}$ or ν_{S-H}. The crystals obtained from carbon tetrachloride or benzene–petroleum ether gave a slightly yellowish coloration and mp 121—123 °C. Recrystallization from methanol or ethanol afforded white crystals with 1/4 molecule of the solvent (mp of the methanol adduct, 80—81.5 °C), which on evacuation at 70 °C over P_2O_5 turned to the same yellowish material. Mass spectra showed M^+ at *m/e* 296 (relative intensity, 19%) and $C_7H_5CO^+$ at *m/e* 105 (100%). In contrast to the IR spectra in solid state, the solution spectra in chloroform show a strong carbonyl band at 1675 cm^{-1} indicating the presence of normal functional group for ArSCOPh. In the ^{1}H NMR spectra in $CDCl_3$, only a sharp singlet for S–H (1H, δ 3.97 from TMS) was present besides the complex multiplets for aromatic protons (11H, δ 7.05—8.15). The sample recrystallized from methanol and ethanol showed additional broad singlets for O–H protons centered at δ 2.60 and δ 3.05, respectively, as well as the normal proton signals for methyl and ethyl groups. The signal for S–H was not affected appreciably by the presence of alcohol when the measurements were made at relatively low sample concentrations (5%). The results indicate that monobenzoylated 1,8-naphthalenedithiol can exist in two isomeric forms, 8-benzoylthio-1-naphthalenethiol (**1**) and 2-phenylnaphtho[1,8-*de*][1,3]dithian-2-ol (**2**). The latter is isolable as solid only by a fortuitous stabilization in the crystal lattice, the former structure being energetically favorable in solution.



A similar attempt for the preparation of the monoacetyl derivative by the reaction with acetic anhydride yielded a viscous oil after purification on silica gel (25% yield as monoacetate).[1] This preparation gave the exact result in elemental analysis for the expected thioester. However, the IR spectra (neat) showed only a weak carbonyl band at 1690 cm^{-1} and strong ν_{O-H} band at 3300 cm^{-1}, indicating the presence of substantial amount of O–H containing species. Thus, the NMR spectra in $CDCl_3$ consist of two sets of signals, which most probably arise from the two structural isomers **3** and **4** (Fig. 1), analogous to those for the monobenzoate derivative. In contrast to the benzoyl derivative, the cyclic isomer **4** is more favored as compared to **3** in the ratio *ca.* 4: 1. This is understandable if we recall the fact that the resonance stabilization associated with the conjugation between carbonyl and phenyl groups is eliminated on going from **1** to **2**. The equilibrium is also dependent on the nature of the solvent. In deuteriated methanol only one species, probably **4**, was observed in the NMR spectrum (one methyl signal in the high-field side, δ 2.03; however, the possibility that the two isomers are in rapid equilibrium in NMR time scale can not be excluded), and the carbonyl band at 1670 cm^{-1} was very weak in intensity. It is reasonable that the hydroxylic medium favors the formation of **4**, since the latter would be more stabilized than **3** in virtue of hydrogen bonding interaction with the solvent.

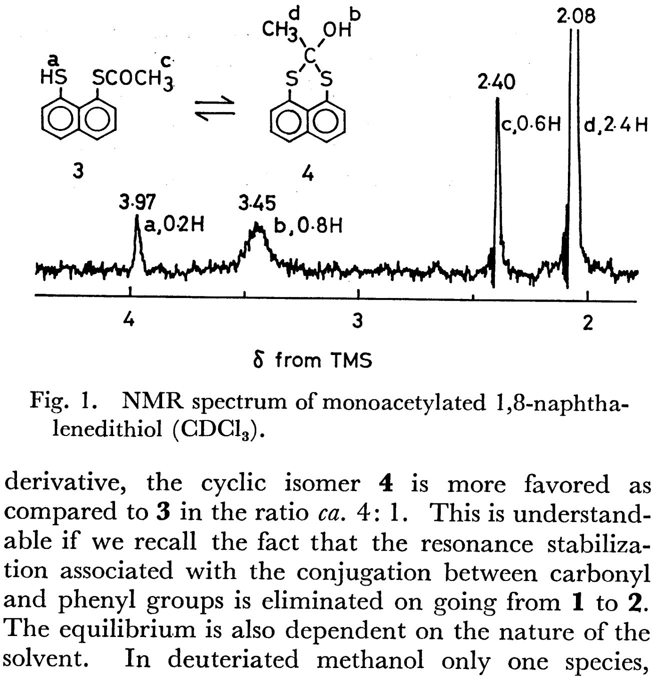
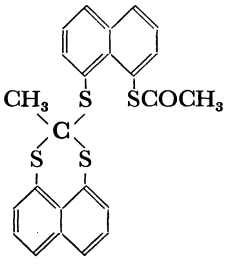


Fig. 1. NMR spectrum of monoacetylated 1,8-naphthalenedithiol ($CDCl_3$).

Another property related to the stability of the cyclic structure is the behavior in a strong acid. As an example, **3** (**4**) dissolves in 96% sulfuric acid with intense bluish-violet coloration, showing a single methyl signal at δ 2.75 (ppm from external TMS) and multiplet at δ 7.0—8.0. The former is featured by a considerable down-field shift as compared to that of **3** or **4**. Dilution of the solution with cold water gave only a trace of recovered **3** (**4**), affording **5** as white crystalline solid. Compound **5** (mp 130—131 °C; $\nu_{C=O}$, 1690 cm^{-1}; NMR in $CDCl_3$, δ 1.78 (s, 3H), 2.23 (s, 3H), 7.1—8.0 (m, 12H), confirmed also by EA and molecular weight measurement by osmometer) was isolable as a by-product by monoacetylation in 20% yield. This is presumably formed by acid catalysed bimolecular condensation of **3** and **4** during the course of isolation. The solution of **5** in H_2SO_4 gave identical NMR signals to those of **3** (**4**). Though the evidences are preliminary, they seem to indicate the formation of carbenium ion **6**2) in sulfuric acid solution.



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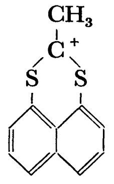

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It is interesting that the structures of **2** and **4** embody the tetrahedral addition intermediate from the ester (RCOSR') and the nucleophile (R'SH) of interest in acyl transfer mechanism, whose isolation and characterization have only recently been successfully carried out for a specifically designed polyfunctional compound directed to the study of enzyme-like catalysis for acyl transfer processes.3) The facile formation of the tetrahedral intermediate for the present compounds is undoubtedly related to the unique spatial disposition of the two aromatic thiyl groups around the hemiacylal carbon. For the monoacylated analogues derived from aliphatic 1,3-dithiols,4) no such intermediates were detected.5)

References

1) A photochemical method has been described for the preparation of monoacyl derivative of 1,8-naphthalenedithiol (Ref. 4), but the ordinary acylation practice proved to be more convenient for large scale synthesis.

2) **6** seems to be the first example of dithiyl-substituted carbenium ion from 1,8-naphthalenedithiol.

3) G. A. Rogers and T. C. Bruice, *J. Am. Chem. Soc.*, **96**, 2481 (1974).

4) M. Takagi, S. Goto, and T. Matsuda, *J. Chem. Soc., Chem. Commun.*, **1976**, 92.

5) In sulfuric acid, however, the aliphatic analogues were found to behave somewhat similarly. 1,3-Dithiol is a structural unit of coenzyme dihydrolipoic acid which functions as an acetyl carrier in pyruvate dehydrogenase. In this connection, thermodynamic stability of the tetrahedral addition intermediate exhibited by mono-*S*-acetylated 1,8-naphthalenedithiol should not be overlooked. However, implications based on a simple structural analogy between the aromatic and aliphatic 1,3-dithiols should not be made.