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# DIMER OF 2-PYRIDYL ISOTHIOCYANATE (1)

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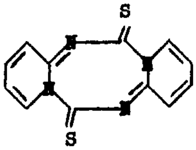
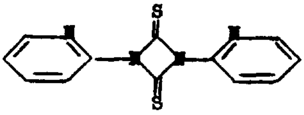
In connection with our investigation of the new and interesting class of compounds, the imidoyl isothiocyanates (2), we have determined the structure of the red 2-pyridyl isothiocyanate dimer (3,4). While previous investigators (3) have concluded that the eight-membered ring (I) was more consistent with the physical evidence, particularly the infrared spectrum, than the alternative structure (II), no mention was made of 3-(2-pyridyl)-pyrido[1,2-a]-s-triazine-2,4-dithione (III) as a third possibility. The formation of III from two isothiocyanate molecules, as symbolized in (1), may be formally regarded as a Diels-Alder reaction in which the -N=C=S function serves as the dienophile and the

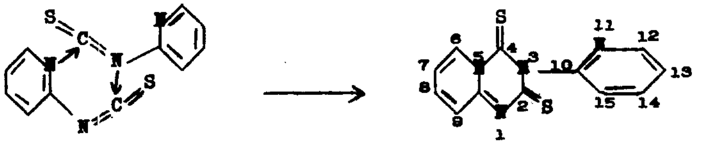


I



II

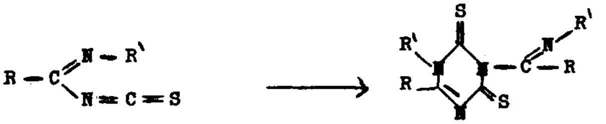
$-\overset{|}{N}{=}C{-}N{=}C{=}S$ system as the diene. Indeed, imidoyl isothiocyanates (2)



(1)

III (5)

(IV) spontaneously dimerize (6) in exactly this manner to orange-red solids (V), e.g. N-methylbenzimidoyl isothiocyanate (IVa) dimerizes readily to 1-methyl-3-(α-methyliminobenzyl)-6-phenyl-s-triazine-2,4-dithione (Va). The structural assignment of Va is based on the presence of two singlet signals (3:3 ratio) in the n.m.r. spectrum (7) at 224 and

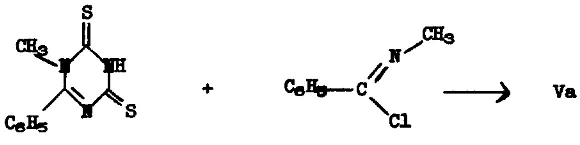


(2)

IV V

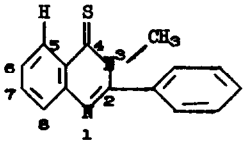
IV, V, R = aromatic, R' = aromatic, aliphatic
IVa, Va, R = $C_6H_5$, R' = $CH_3$

243 c.p.s. attributable to the protons situated on the two N-$CH_3$ groups, and on independent synthesis via the interaction of 1-methyl-6-phenyl-s-triazine-2,4(3H)-dithione (VI) (8) with N-methylbenzimidoyl chloride (VII) in pyridine. These findings provided a useful groundwork for the


VI VII (3)

structural elucidation of the 2-pyridyl isothiocyanate dimer since other isothiocyanate dimers have not been heretofore reported.

The proposed structure (III) of the 2-pyridyl isothiocyanate dimer is substantiated by n.m.r. (9) spectral data. A proton ratio of 1:1:2:4 was obtained in ascending field strength, and from representative examples an unambiguous assignment for the protons could be made. The assignment of the doublet signal at lowest field, centered at 557 c.p.s. (10), to the proton on $C_8$, peri to the thiocarbonyl group, was based on the values and splitting patterns of similarly situated protons in 4-quinazolinethiones (2) such as VIII (11). With respect to VIII, the doublet signal of the proton on $C_5$ was at the lowest field, centered at 536 c.p.s. ($J_{5,6} \cong 7.8$) (7,12), and its splitting pattern was very similar to that of the proton on $C_8$ of the dimer (III). The doublet signal centered at 517 c.p.s. (10), which was attributed to the proton on $C_{12}$ of the dimer (III), as well as the signals attributed to the protons on $C_{13}$, $C_{14}$, and $C_{15}$, was assigned in accordance with the values and splitting patterns of similarly located protons in both 2-pyridyl isothiocyanate (13) and 2-aminopyridine (14). The spin coupling constants


VIII

for the proton on $C_6$ are $J_{6,7} \cong 7.7$, $J_{6,8} \cong 1.1$, and $J_{6,9} \cong 0.5$ c.p.s. (12). Those for the proton on $C_{12}$ are $J_{12,13} \cong 4.7$, $J_{12,14} \cong 2.0$, and $J_{12,15} \cong 1.0$ c.p.s. (12). The overlapping signals for the protons on $C_9$ and $C_{14}$ (15) were a multiplet centered at approximately 484 c.p.s. (24 c.p.s. approximate width) and those for the protons on $C_7$, $C_8$, $C_{13}$, and $C_{15}$ were a multiplet centered at approximately 445 c.p.s. (30 c.p.s. approximate width). Neither of the alternative structures, (I) and (II), for the 2-pyridyl isothiocyanate dimer corresponds to the n.m.r. spectral data. Structure I is inconsistent with the recorded proton ratio, while II, in addition to this factor, would not be expected to show a signal at 557 c.p.s.

Acknowledgement. — We are deeply indebted to Mr. L. Dorfman, Miss N. Cahoon, and Miss J. Siragusa for their valuable contributions in recording and interpreting n.m.r. spectra.

## References

1. Acceptable elemental analyses were obtained for all new compounds encountered in this investigation.
2. Presented in part by H. M. Blatter at the 145th National Meeting of the American Chemical Society, New York, New York, September, 1963, p. 89Q of the abstracts.
3. J. C. Howard and J. G. Michels, J. Org. Chem., **25**, 829 (1960).
4. A. E. S. Fairfull and D. A. Peak, J. Chem. Soc., 796 (1955).
5. This numbering system avoids the numeral duplication inherent in the nomenclature.

6. J. Goerdeler in a recent lecture, Angew. Chem. Intern., Ed. Engl., 2, 693 (1963), mentioned the dimerization of imidoyl isothiocyanates to compounds he assumed were s-triazines, but details have not been given.

7. The n.m.r. spectrum was determined on a Varian A-60 spectrometer in deuteriochloroform. Values are given in c.p.s. relative to tetramethylsilane as internal standard.

8. Prepared from 1-methyldithiobiuret by the ring closure procedure of A. E. Fairfull and D. A. Peak, J. Chem. Soc., 803 (1955).

9. The n.m.r. spectrum was determined on a Varian A-60 spectrometer in dimethyl-$d_6$-sulfoxide. Values are given in c.p.s. relative to tetramethylsilane as internal standard.

10. In deuteriochloroform the two lowest field signals were centered at 559 and 524 c.p.s.

11. We wish to thank Professor L. Legrand, Caen, France, for a sample of compound VIII.

12. The values for the spin coupling constants were obtained from a first order treatment of the curve, and as a result only approximate values were given.

13. The dimer (III) is stable at room temperature in dimethyl-$d_6$-sulfoxide, but dissociates to the monomer on heating for five minutes on a steam bath, as evidenced by the red to yellow color change and the complete change in the n.m.r. spectrum. The spectrum now shows the loss of the doublet signal at 557 c.p.s. attributed to the proton on $C_6$ of the dimer (III) and a proton ratio of 1:1:2 in ascending field strength. It shows a doublet signal indicative of ortho splitting centered at 510 c.p.s. with each signal split into an unsymmetrical quartet, and multiplets centered at approximately 477 c.p.s. (20 c.p.s. approximate width) and approximately 446 c.p.s. (20 c.p.s. approximate width). The splitting patterns are very similar to those of 2-aminopyridine (14). 2-aminopyridine shows a proton ratio of 1:1:2 in ascending field strength with the signals attributed respectively to the proton on $C_6$ followed by the proton on $C_4$ which is in turn followed by the $C_3$ and $C_5$ protons which overlap.

14. "N.M.R. Spectra Catalog", compiled by N. S. Bhacca, D. P. Hollis, L. F. Johnson, and E. Pier of the Instrument Division of Varian Associates, Palo Alto, California, Vol. 2, Spectrum No. 431 (1963).

15. The positions assigned to the protons on $C_{14}$ and $C_{15}$ might actually be reversed because of the unknown anisotropy effects of the thiocarbonyl groups at $C_2$ and $C_4$.