the acetones with longer times of reaction). Likewise, Type III materials could be prepared from I using toluenesulfonic acid, but such were not observed using this catalyst with the acetone compounds. These results indicate that the carbonyl carbon atom of I is less electropositive than that in the fluorochloroacetones, resulting in a weaker carbon-oxygen bond in Type II compounds derived from I, with consequent easier formation of Type III derivatives from I. This situation results from the higher electronegativity of the fluorine atom compared with that of chlorine. Similarly, I easily forms Type III derivatives from hydrocarbons with $AlCl_3$ as catalyst, while the acetone compounds have been observed to form only Type II derivatives (*1*) from hydrocarbons.

Ketones with a relatively electronegative carbonyl carbon atom, on the other hand, apparently form only Type III derivatives from phenols under the conditions employed to date (*6*, *7*).

ACKNOWLEDGMENT

We are indebted to J. P. Sibilia for the N.M.R. study of IIIa.

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RECEIVED for review September 9, 1965. Accepted February 1, 1966.

Nuclear Magnetic Resonance Spectra of 1,2-Dithiole-3-thiones

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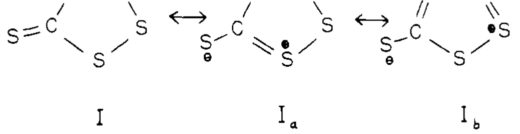
Nuclear magnetic resonance spectra are recorded for various aryl- and alkyl-substituted 1,2-dithiole-3-thiones and their carbonyl analogs. By examining the spectra of known compounds, resonance field positions have been assigned for hydrogen or methyl groups attached at either the 4- or 5- position in the 1,2-dithiole-3-thione ring system. Protons in the 4- position give a resonance at 2.6 to 2.8*t* while protons in the 5-position show a resonance at 1.6 to 1.7*t*.

THE 1,2-dithiole-3-thione ring system is recognized as pseudoaromatic (*4*). This is the result of the contributions of the sulfur electrons, which coupled with the carbon-carbon double bond electrons provide six electrons to satisfy the Huckel rule for aromaticity. While crystallographic studies have provided some details on the resonance contributions of structures I, Ia, and Ib (*2*), there has been little work on the use of nuclear magnetic resonance as a tool to evaluate the nature of protons attached to the dithiole ring and to substantiate structural assignments.

In the course of synthetic work on dithioles, the NMR spectra of a number of 1,2-dithiole-3-thiones substituted in the 4- and 5- positions by alkyl and aryl groups were measured and tabulated. Generalizations with possible analytical value are drawn from the data and some suggestions are made regarding the observed chemical shifts and spin coupling constants.



I I_a I_b

EXPERIMENTAL

Nuclear magnetic resonance spectra were taken on 10 weight % solutions of the organic compound in carbon tetrachloride using a Varian A-60 instrument. Concentrations greater than 10% showed appreciable shifts to higher fields for the individual proton resonances, but lower concentrations had negligible effects. All measurements were made using tetramethylsilane as an external reference.

5-Phenyl-1,2-dithiole-3-thione (m.p. 122° C.) (*1*), 5-phenyl-1,2-dithiole-3-one (m.p. 117–18° C.) (*1*), and 4-phenyl-1,2-dithiole-3-thione (m.p. 122–23° C.) (*3*), were prepared by previously reported procedures. 4-Neopentyl-5-*tert*-butyl-1,2-dithiole-3-thione (b.p. 152° C. at 1 mm.) was obtained from the reaction of triisobutylene with sulfur (*5*). 4-Methyl-1,2-dithiole-3-thione (m.p. 40–41° C.) 4-methyl-5-*tert*-butyl-1,2-dithiole-3-thione (m.p. 79–80° C.), and 4-neopentyl-1,2-dithiole-3-thione (m.p. 85–86° C.), were obtained by the method of Spindt, Stevens, and Baldwin (*7*). 1,2-Dithiole-3-thione was prepared by the method of Mayer and Kubasch (*6*).

4-Phenyl-1,2-dithiole-3-one. Six grams (0.028 mole) of 4-phenyl-1,2-dithiole-3-thione was dissolved in 150 ml. of acetone and to the stirred solution a solution of 9.6 grams of $KMnO_4$ in 150 ml. of acetone was added in 1 hour. When the solution was concentrated to 50-ml. volume and cooled, orange crystals which melted at 118–19° C. were obtained.

Analysis. Calculated for $C_9H_6S_2O$: C, 55.64; H, 3.11; S, 33.01. Found: C, 55.60; H, 3.12; S, 33.21.

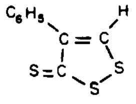
5-Methyl-1,2-dithiole-3-thione. Sixty-four grams of sulfur was placed in a cylindrical reactor fitted with a stirrer, a coarse fritted-glass gas inlet tube, and a liquid take-off trap connected to an efficient condenser. The sulfur was stirred and heated at 200° C. and 2-butene gas was passed through the system at a rate of 50 ml. per minute for 20 hours. By-product H_2S was vented to a hood while liquid and solid condensate collected in the take-off trap. Twenty grams of condensate was collected and recrystallized five times from hexane to give yellow crystals (m.p. 33° C.).

Analysis. Calculated for $C_4H_4S_3$: C, 32.40; H, 2.72; S, 64.88; mol. wt. 148.2. Found: C, 32.21; H, 2.68; S, 64.86; mol. wt. (mass spectrometer) 148.

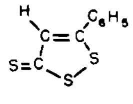
RESULTS AND DISCUSSION

The NMR spectra of seven 1,2-dithiole-3-thiones are summarized in Table I. The spectrum of the parent compound, 1,2-dithiole-3-thione (I), has a pair of doublets at 1.62*t* and 2.79*t* with a coupling constant of 6 c.p.s. The high field doublet is assigned to the 4-proton based on comparisons with the chemical shifts observed for the 4-protons in 5-methyl-1,2-dithiole-3-thione (III) and 5-phenyl-1,2-dithiole-3-thione (V). In all three cases the 4-proton shift occurs at 2.62 to 2.79*t*. Confirming this assignment, the 5-proton in 4-methyl-1,2-dithiole-3-thione (III) and 4-phenyl-1,2-dithiole-3-thione (IV) has a chemical shift in the 1.60- to 1.73-*t* region. The coupling constant of 6 c.p.s. for the C_4-C_5 protons in I is in the range of values reported for aromatic orthohydrogens.

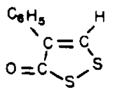
4-Phenyl-1,2-dithiole-3-thione, 5-phenyl-1,2-dithiole-3-thione, and their carbonyl analogs (VI and VII) all show multiple aryl proton reasonance in the 2.25- to 2.67-*t* region. The center of the resonance in the 4-phenyl derivatives (IV and VI), occurs at slightly higher fields than in the 5-phenyl derivatives (V and VII).



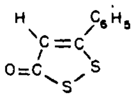
IV



V



VI



VII

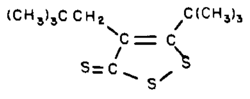
Examination of the chemical shift for the proton attached to the heterocyclic ring in each of the four compounds shows a similar shift related to the proximity of the thiocarbonyl or carbonyl group. In this case, the resonances for the 4-proton in the 5-phenyl derivatives (V and VII) occur at higher field than their corresponding 5-proton in the 4-phenyl derivatives (IV and VI). These shifts, consistent with the smaller shifts observed with the phenyl protons, are what one would predict from an α,β-unsaturated compound. This deshielding is absent from V and VII; in fact, a slight upfield shift is observed as would be predicted on the basis of polarization of the α,β-unsaturated compound.

Table I. Chemical Shift Data on 1,2-Dithiole-3-thiones and 1,2-Dithiole-3-ones[a]

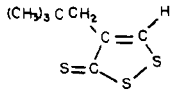
Compound	τ, P.P.M.	Splitting	Assignment
I	2.79	Doublet	4-H
	1.62	Doublet	5-H
II	1.60	Quartet	5-H
	7.67	Doublet	4-CH_3
III	2.62	Quartet	4-H
	7.32	Doublet	5-CH_3
IV	1.73	Singlet	5-H
	2.64	Multiplet	4-Ph
V	2.68	Singlet	4-H
	2.25	Multiplet	5-Ph
VI	2.20	Singlet	5-H
	2.67	Multiplet	4-Ph
VII	3.14	Singlet	4-H
	2.35	Multiplet	5-Ph
VIII	8.54	Singlet	CH_3 of 5-*tert*-butyl
	8.90	Singlet	CH_3 of 4-neopentyl
	6.88	Singlet	4-CH_2-
IX	8.98	Singlet	CH_3 of 4-neopentyl
	6.90	Singlet	4-CH_2-
X	8.43	Singlet	CH_3 of 5-*tert*-butyl
	7.64	Singlet	4-CH_3

[a] Measurements made as 10 weight % solutions in CCl_4 using tetramethylsilane as reference.

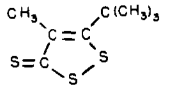
The NMR spectrum of 4-neopentyl-5-*tert*-butyl-1,2-dithiole-3-thione (VIII) has previously been used to support the assigned structure (*5*). This compound has two nearly equal intensity resonances (methyl groups) at 8.90 and 8.43*t*. The methylene protons have a resonance at 6.88*t*. The high field resonance can be assigned to the methyl protons of the neopentyl group and the low field resonance to the methyl protons of the *tert*-butyl group. These assignments are based on comparisons of the NMR spectra of the isomeric thiones, 4-neopentyl-1,2-dithiole-3-thione (IX) and 4-methyl-5-*tert*-butyl-1,2-dithiole-3-thione (X). Once again, the proximity of the thiocarbonyl group is associated with an upfield shift.



VIII



IX



X

The resonances of the methylene protons of VIII and IX occur in the region characteristic of benzyl methylenes and the resonance for the methyl group of X is consistent with reported values for a methyl group attached to an aromatic ring.

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RECEIVED for review October 21, 1965. Accepted March 3, 1966.