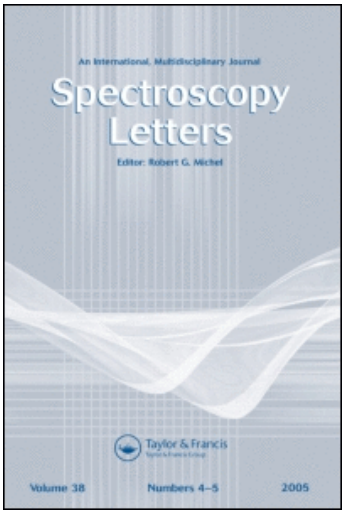

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

THE REACTION OF 5-METHYL-3-(*o*-TOLYL)RHODANINE WITH ACETONE-d_6 AND METHANOL

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Online publication date: 31 May 2001

To cite this Article Doğan, İlknur and Yaman, Arzu(2001) 'THE REACTION OF 5-METHYL-3-(*o*-TOLYL)RHODANINE WITH ACETONE-d_6 AND METHANOL', Spectroscopy Letters, 34: 3, 365 — 370
To link to this Article: DOI: 10.1081/SL-100002291
URL: http://dx.doi.org/10.1081/SL-100002291

SPECTROSCOPY LETTERS, 34(3), 365–370 (2001)

THE REACTION OF 5-METHYL-3-(*o*-TOLYL)RHODANINE WITH ACETONE-d_6 AND METHANOL

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ABSTRACT

5-Methyl-3-(*o*-tolyl)rhodanine was found to react with acetone-d_6 and methanol at the 5-position of the heterocyclic ring. The reactions have been followed and the products have been identified by ^{1}H NMR.

Key Word: 5-Methyl-3-(*o*-tolyl)rhodanine.

INTRODUCTION

Tautomerization of the rhodanine ring has attracted attention both theoretically (1) and experimentally (2). We have been working on the internal hindered rotation in N-(*o*-aryl) substituted rhodanines (3,4,5) where the hindered rotation around the $N_{(sp_2)}$-$C_{(aryl)}$ bond causes the formation of resolvable (4) enantiomers. Now we extend our research to N-(*o*-aryl) substituted 5-methyl rhodanines (Fig. 1) where the hindered rotation will form diastereomers (6). Rang *et al* studied the racemization of the rhodanine ring *via* enolization and concluded that the 5-alkyl

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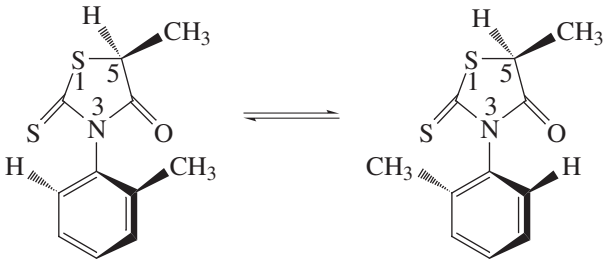

Figure 1. The thermally interconvertable rotational isomers of 5-methyl-3-(*o*-tolyl)-rhodanine.

rhodanines were optically stable in neutral solvents which meant for us that the racemization mechanism for our compounds (Fig. 1) will be via rotation around the $N_{(sp2)}$-$C_{(aryl)}$ bond.

As an implication of slow tautomerization of the rhodanine ring on the other hand, we observed a slow reaction of 5-methyl-3-(*o*-tolyl) rhodanine with acetone-d_6 and with methanol which will be reported in this paper.

RESULTS AND DISCUSSION

Reaction with Acetone-d_6

5-methyl-3-(*o*-tolyl)rhodanine has been synthesized by the reaction of *o*-tolylisotiocyanate with ethylthioglycolate, its purity has been checked and the compound has been fully characterized (6). The 60 MHz ^{1}H NMR spectrum of the compound (7) taken in acetone-d_6 showed the presence of a doublet at 1.7 ppm due to the presence of the methyl group at 5 position of the ring, a siglet at around 2 ppm due to the *ortho* methyl protons, a quartet at 4.6 ppm due to the methine proton and the aromatic protons at about 7.1 ppm (Fig. 2). The solution was kept in the NMR tube at 25°C and spectra were taken at regular time intervals. It has been observed that after 7 days the quartet at 4.6 ppm that had been assigned to the methine proton at the 5-position of the heterocyclic ring disappeared. The disappearance of the quartet was accompanied with the conversion of the doublet which was assigned to the protons of the methyl group at 5 position, to a singlet (Fig. 2). This result has been interpreted in terms of the reaction of 5-methyl-3-(*o*-tolyl)rhodanine with acetone-d_6 at 5-position of the heteroring. The reaction probably took place *via* enolization of the rhodanine ring (Scheme 1).

When the reaction mixture was acidified with trifluoroacetic acid, the original signals of the 5-methyl-3-(*o*-tolyl)rhodanine reappeared (Fig. 2), which showed

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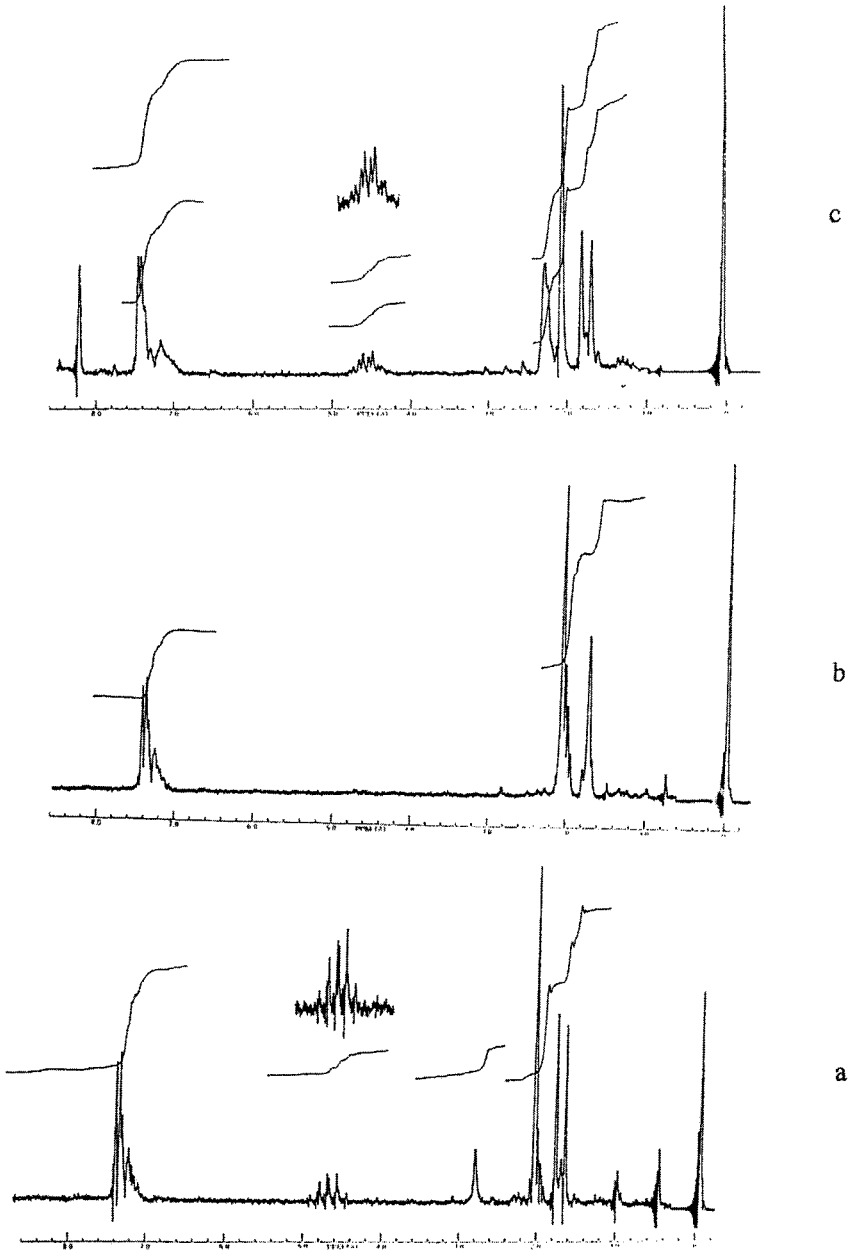

Figure 2. The 60 MHz ^{1}H NMR spectrum of 5-methyl-3-(*o*-tolyl)rhodanine in acetone-d_6. a: before reaction, b: after reaction with acetone-d_6, c: after addition of CF_3COOH.

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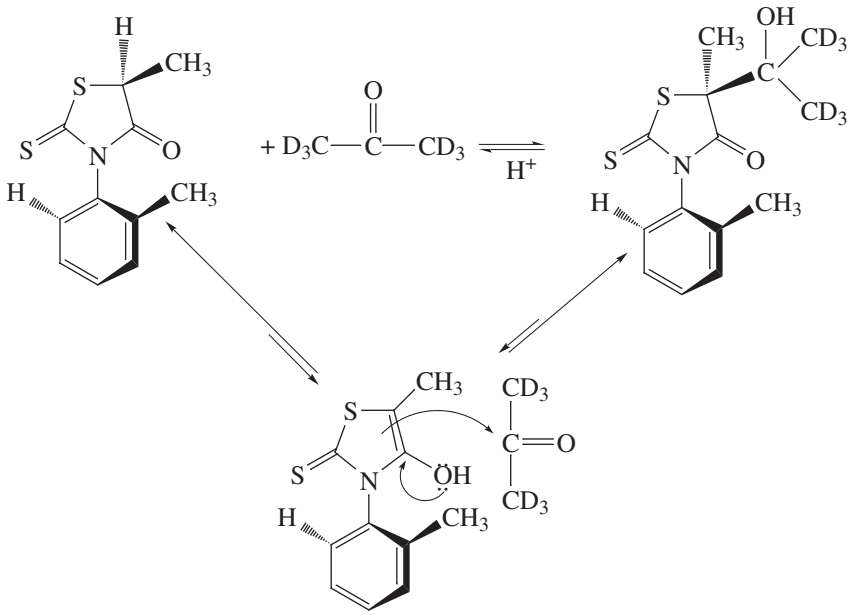


Scheme 1. The reaction of 5-methyl-3-(*o*-tolyl)rhodanine with acetone-d_6 shown on one of the diastereomers.

that the reaction was reversible in acid. A similar reaction had been observed for the 5-methylene protons of barbituric and 2-thiobarbituric acids (8).

The reaction with acetone-d_6 was also carried out with 3-(*o*- tolyl)rhodanine and with 5,5-dimethyl-3-(*o*-tolyl)rhodanine as well, however no reaction has been observed under the same reaction conditions. The fact that no reaction has been observed for the 5,5-dimethyl derivative, where there is no chance for tautomerization of rhodanine, supports our interpretation of the reaction with acetone-d_6 at the 5 position of the ring via enolization. Observation of no reactivity for the rhodanine unsubstituted at position 5 shows that substitution at this position increases the reactivity. In fact a higher rate of enolization had been observed for the 5-phenylrhodanine studied in reference 2.

Reaction with Methanol

The ^{1}H NMR spectrum taken in deuterochloroform after 5-methyl-3-(*o*-tolyl)rhodanine was refluxed in methanol for 5 days, followed by evaporation of the methanol showed that the compound reacted with methanol at 5-position of

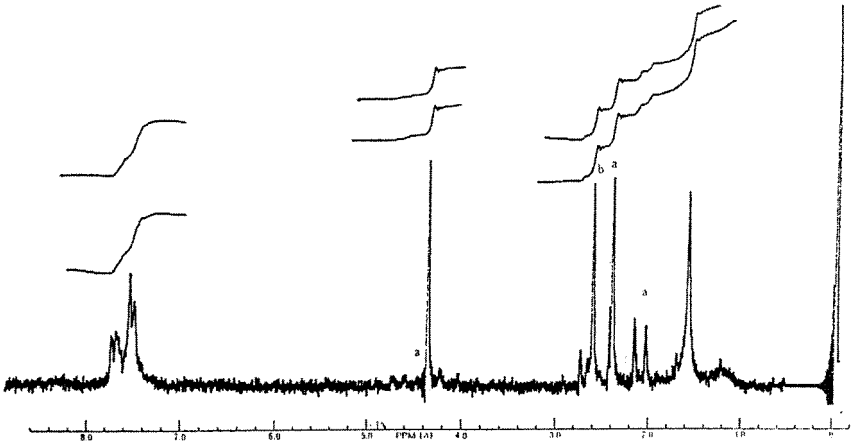
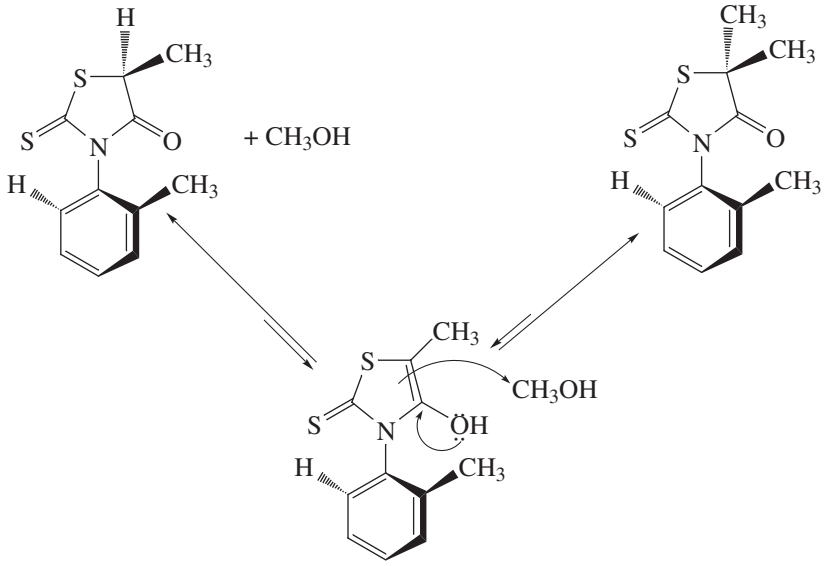


Figure 3. The 60 MHz ^{1}H NMR spectrum of 5-methyl-3-(*o*-tolyl)rhodanine in CCl_4 after reaction with methanol. [a]Signals due to unreacted rhodanine, [b]signals due to the product shown in scheme 2.



Scheme 2. The reaction of 5-methyl-3-(*o*-tolyl)rhodanine with methanol shown on one of the diastereomers.

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the heterocyclic ring to give 5,5-dimethyl-3-(*o*-tolyl)rhodanine. The product was obtained together with some unreacted reactant (Fig. 3) so that the spectrum obtained contained the two superimposed spectra. The additional singlets which appeared after the reaction at 2.2 ppm and 2.3 ppm have been assigned to the *o*-methyl and the two methyl groups at 5-position of the ring, respectively. The mechanism of the reaction of the compound with methanol is thought to involve tautomerization of the rhodanine ring as shown in Scheme 2. No such reaction has been observed with ethanol.

APPARATUS

Proton NMR spectra were recorded on a Bruker AC-200 (200 MHz, T = 23°C) or on a Varian T-60 A NMR (60 MHz, T = 23°C).

ACKNOWLEDGMENT

We thank to Bogaziçi University research fund for their financial support (project No: 99B509).

REFERENCES

1. Enchev V., Petkov I., Chorbadjiev S. Structural Chemistry 1994; 5(4): 225.
2. Rang K., Isaksson R., Sandström J. J. Chem. Soc., Perkin Trans. 2, 1996; 1493.
3. Doğan İ., Burgemeister T., Içli S., Mannschreck A. Tetrahedron 1992; 48: 7157.
4. Doğan İ., Pustet N., Mannschreck A. J. Chem. Soc., Perkin Trans. 2, 1993; 1557.
5. Karataş M., Koni S., Doğan İ. Can. J. Chem. 1998; 76: 254.
6. Doğan İ., Yaman A. Manuscript in preparation.
7. For this compound, 250 MHz ^{1}H NMR spectrum shows the presence of diastereomeric peaks which is reported in the paper cited in reference 6.
8. Oğuz F., Doğan İ. Spectroscopy Letters. 1998; 31(2): 469.

Received November 28, 2000
Accepted January 10, 2001

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