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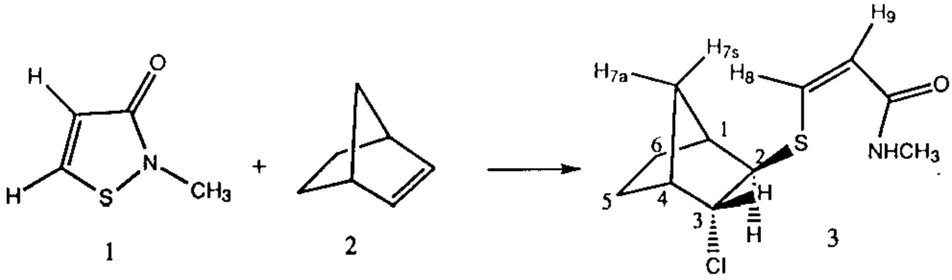
GENERATION AND TRAPPING OF A SULFENYL CHLORIDE FROM AN ISOTHIAZOLONE

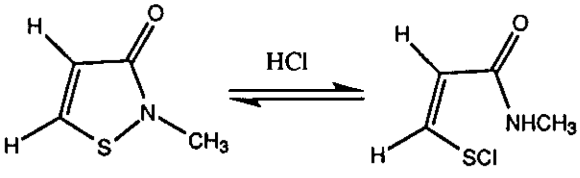
Tirthankar Ghosh* and Steven K. Wolk[a]

Rohm and Haas Research Laboratories, 727 NorristownRoad,
Spring House, PA 19477, U.S.A.

Abstract - We have investigated the reaction of HCl with 2-methylisothiazol-3-one (**1**). In the presence of HCl, at elevated temperatures, **1** exists in equilibrium with the ring opened sulfenyl chloride (**4**). The existence of **4** has been proven by trapping with norbornene and 1-octyne.

When a solution of 2-methylisothiazolin-3-one (**1**)[1] in 2-propanol was heated with aqueous HCl at 80°C for several hours, no degradation was observed. However, when the same experiment was carried out in the presence of excess norbornene (**2**), the chlorosulfide (**3**) was obtained as the only major product in 20% yield.[2] The regio- and stereochemistry of **3** was determined by using nmr spectroscopy, including ^{1}H nmr, ^{13}C nmr, and two-dimensional techniques (COSY, HMQC, and HMBC).[3] Unambiguous assignment of C_2 substituent was based on a three-bond ^{1}H/^{13}C J-coupling to H_8 observed in the HMBC spectrum. A four-bond W-coupling was observed between H_2 and H_{7a} indicating the *exo* orientation of the sulfur substituent. Similarly, an absence of a coupling between H_3 and H_{7a} and a presence of coupling between H_3 and H_4 indicated the endo orientation of the C_3 substituent. This result indicates that, in the presence of HCl, **1** is in equilibrium with the ring opened sulfenyl chloride derivative (**4**). In the presence of norbornene the sulfenyl chloride is selectively trapped to give **3**. Arenesulfenyl chlorides are known to add to norbornene to give **5**.[4]





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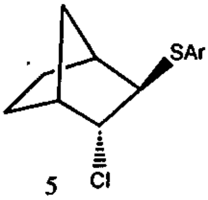

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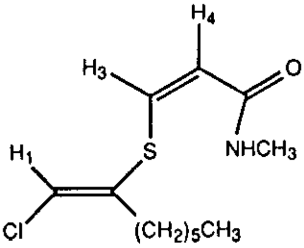
The presence of **4** was also proved by trapping with 1-octyne. Unlike the trapping with norbornene, this reaction gave four isomeric products (isolated yield of 25%) in a ratio of 60:22:12:8. The same techniques described for the norbornene derivative characterization were used to assign the structures of the two dominant species. The key to the assignments were the J-couplings observed in the HMQC and HMBC spectra. For example, in **6** (60%), C_2 showed a three-bond coupling to H_3 in the HMBC spectrum, while C_1 showed a one-bond coupling to H_1 in the HMQC spectrum, showing that the sulfur and H_1 were bound to different vinyl carbons. Compound (**6**) is formed by a trans *anti*-Markovnikov addition of **4** where as **7** is formed by a trans Markovnikov addition. The preference of the *anti*-Markovnokov product with trans stereochemistry has precedence.[5] The structures of the remaining two products have not been assigned due to lack of cross peaks from these species in the 2D nmr spectra. These could be products arising from cis addition of **4** to 1-octyne.



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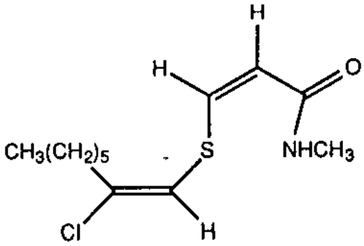

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All attempts to observe **4** directly by heating a solution of **1** in isopropanol-d_8 in the probe of an nmr spectrometer were unsuccessful. When some norbornene was added to this mixture we were able to observe the formation of **3**.

This study has shown that HCl adds across the S-N bond of isothiazolones to provide the corresponding ring opened sulfenyl chloride which can be trapped by alkenes and alkynes. Studies are under way to determine the generality and scope of this reaction.

[a] For details of the nmr analysis please contact S. K. Wolk.

REFERENCES

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2. For **3**: ^{1}H Nmr, δ 7.00 (d, J=10 Hz, H_8), 6.20 (br s, N-H), 5.98 (d, J=10 Hz, H_9), 4.13 (m, H_3), 2.84 (m, N-CH_3 and H_2), 2.50 (dd, J_1=J_2=3.6 Hz, H_4), 2.30 (d, J=4.2 Hz, H_1), 2.00 (m, H_{5endo}), 1.83 (d, J=10.7 Hz, H_{7syn}), 1.75 (m, $_{6exo}$), 1.49 (m, H_{5exo}), 1.44 (m, H_{7anti}), 1.40 (m, H_{6endo}): ^{13}C Nmr, 166.9 (C=O), 141.9 (C_8), 116.2 (C_9), 68.5 (C_8), 59.6 (C_2), 44.3 (C_4), 43.6 (C_1), 35.7 (C_7), 28.9 (C_6), 26.0 (N-CH_3), 21.5 (C_5) ppm; ir (neat), 3300, 3100, 2980, 2260, 1640, 1580, 1420, 1260, 1200, 940, 800, 740 cm^{-1}. Molecular weight from mass spectrum is 245.
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4. S. Braverman, *The Chemistry of Sulfenic Acids and Their Derivatives*; Patai, S. Ed.; John Wiley and Sons, Inc.; New York, 1990, pp. 340-343.
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