

S. D. Ziman

Chevron Chemical Company, Ortho Division, 940 Hensley Street, Richmond, California 94804

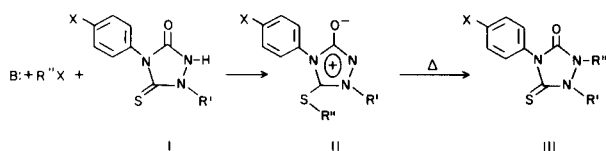
Received February 15, 1980

In the course of preparing some 1,2-dialkyl-4-aryl-5-thioxo-1,2,4-triazolin-3-ones (III) (1), we were looking for a route which would eliminate the problem associated with (a) preparation of 1,2-dialkyl hydrazines and (b) specificity in addition to the isothiocyanate or isocyanate when the alkyl groups were not the same.

J. Heterocyclic Chem., **17**, 1319 (1980).

During this work, we were able to isolate a new meso ionic system (II) (2), and thermally rearrange it to the desired product (Scheme I). This reaction, though given here for only one case, appears to be quite general. The temperature needed for rearrangement is dependent on R'', but in general, when R'' is alkyl, refluxing dimethylformamide is the solvent of choice.

Scheme I



The structure of II is based on its spectral properties, and by comparison of those properties with III. The nmr of II shows both an *N*-methyl groups. The ir of II shows no carbonyl, but a strong C=N at 1655 cm⁻¹; however, the final product has a distinctive carbonyl at 1755 cm⁻¹ which is typical for these structures.

EXPERIMENTAL

The general reaction for the preparation of 1,2-dialkyl-4-aryl-5-thioxo-1,2,4-triazolin-3-ones is illustrated by the following example.

Preparation of 1,2-Dimethyl-4-(4-chlorophenyl)-5-thioxo-1,2,4-triazolin-3-one.

2-Methyl-4-(4-chlorophenyl)-5-thioxo-1,2,4-triazolin-3-one (I) (3) (3.5 g., 0.0145 mole) was added to a solution of 0.78 g.

(0.0145 mole) of sodium methoxide in 100 ml. of methanol and stirred until it went into solution. To this solution was added 2.06 g. (0.0145 mole) of methyl iodide, and the solution was stirred overnight. The methanol was then removed under reduced pressure and the residue taken up in 200 ml. of methylene chloride. It was washed with 100 ml. of water, dried over magnesium sulfate, and the solvent was evaporated under reduced pressure to give a solid. Trituration with ether gave 2.1 g. of a crystalline solid, II; nmr: (ppm) 2.20 (S, 3H), 3.86 (S, 3H), 7.50 (S, 5H); ir 1655 cm⁻¹. The melting point had a range of 130-144°.

Anal. Calcd. for C₁₀H₁₀ClN₃OS: C, 46.97; H, 3.91; N, 16.44. Found: C, 46.78; H, 3.99; N, 16.67.

The intermediate II was dissolved in 25 ml. of dimethylformamide and heated to reflux. The reaction was monitored by nmr. After 18 hours, the rearrangement of II to III was complete. The dimethylformamide was removed by evaporation under reduced pressure, and the product was purified by high pressure liquid chromatography (Waters Prep 500) using 1% ethyl acetate in methylene chloride, giving 1.6 g. of material, m.p. 142-143.5°; nmr (ppm) 3.43 (S, 3H), 3.71 (S, 3H), 7.50 (S, 5H); ir: 1755 cm⁻¹.

Anal. Calcd. for C₁₀H₁₀ClN₃OS: C, 46.97; H, 3.91; N, 16.44. Found: C, 46.96; H, 3.99; N, 16.76.

This reaction can also be carried out in a single step without isolation of II. The alkylation can be done in dimethylformamide using sodium hydride as the base, followed by reflux.

REFERENCES AND NOTES

- (1) For examples of other routes to 5-thioxo-1,2,4-triazolin-3-ones, see (a) German Patent 2,544,866; and (b) U. S. Patent 4,066,437.
- (2) We thank Professor Kevin Potts for his useful discussions on the meso ionic structure, and some of his related work.
- (3) Prepared by reaction of *N,S*-dimethyldithioacetylhydrazide and 4-chlorophenylisocyanate followed by cyclization with sodium methoxide in methanol.