

**Heterocycles: Part VII — Desulphurization of
Triaryl-*s*-trithianes with Hydrazine Hydrate***

JYOTI B. CHATTOPADHYAYA & A. V. RAMA RAO
National Chemical Laboratory, Poona 8

Received 3 July 1974; accepted 12 September 1974

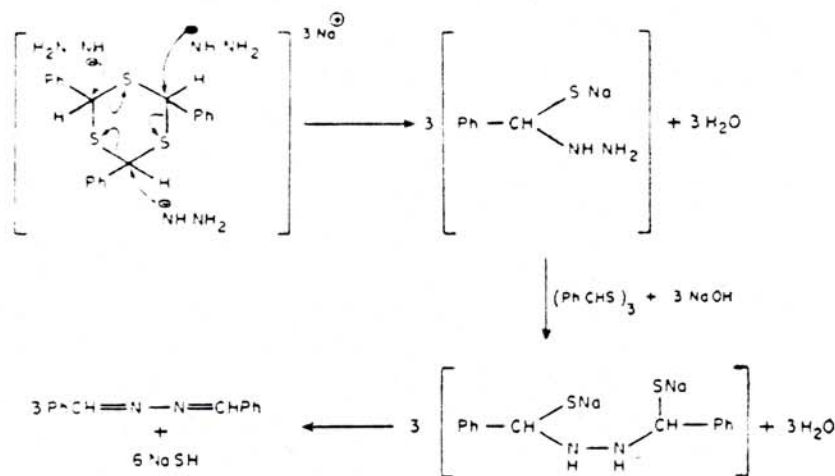
Triaryl-*s*-trithianes can be converted smoothly to the corresponding benzylideneazines by refluxing with hydrazine hydrate and sodium hydroxide in diglyme.

RECENTLY we have reported that *s*-trithianes can be converted to the corresponding carbonyl compounds by iodine and dimethyl sulphoxide¹, silver oxide in aqueous methanol² and iodine and pyridine N-oxide³. It is also known that desulphurization of triaryl-*s*-trithianes by pyrolysis with Raney nickel results in the formation of stilbenes⁴, a method which we have adopted for the synthesis of α, α' -*d*₂-stilbenes⁵.

Hydrazine with or without alkali is known to desulphurize cyclic and acyclic ethylene thioketals to the corresponding hydrocarbons⁶. We now report that triaryl-*s*-trithianes with hydrazine hydrate in the presence of sodium hydroxide effects the desulphurization to give the corresponding benzylideneazines. Thus, when a mixture of triphenyl-*s*-trithiane, 80% hydrazine hydrate and powdered

*NCL Communication No. 1871.

NOTES



SCHEME 1

sodium hydroxide in diglyme was refluxed for a period of 2 hr and worked up, the product obtained was found to be benzylideneazine. The alkali was found to be necessary in all the cases in this reaction, unlike the desulphurization of thioketals⁸. The sulphur was reduced completely to sulphide, which remained in solution, as there was evolution of hydrogen sulphide gas on acidification. When this reaction was repeated with parent trithiane (i.e. *s*-trithioformaldehyde) under similar conditions, the starting material was recovered. The mechanism of the azine formation perhaps involves the thioaldehyde monomer intermediate during some stage of the reaction, to form a hydrazone or by the nucleophilic attack of NH_2NH^- on the electron deficient carbon of the *s*-trithiane ring as depicted in Scheme 1. The stability of triaryl-*s*-trithiane both in refluxing alkaline-dioxane solution and in 80% hydrazine hydrate in diglyme solution leads one to assume that possibly an intermediate such as $\text{NH}_2\text{NH}^-\text{Na}^+$ must be involved in the reaction instead of the hydrazine molecule as such.

Desulphurization of triaryl-trithianes using hydrazine hydrate-alkali — A mixture of triphenyl-*s*-trithiane (3.66 g, 1 mole by weight), hydrazine hydrate (80%, 4 parts by volume), sodium hydroxide (6 moles) in diglyme (13 parts by volume) was refluxed for a period of 2 hr and poured on water. An oil separated out which gradually solidified. The crude solid was homogeneous on TLC, m.p. 92-93° (3 g) and identified as benzylideneazine (lit. m.p. 93°).

Adopting this procedure tri-(*p*-chlorophenyl)-, tris-(3-chlorophenyl) and trianisyl-*s*-trithianes have been converted to 4,4'-dichloro (yield 87%, m.p. 209-11°), 3,3'-dichloro (83%, m.p. 40°) and 4,4'-dimethoxy (89%, m.p. 168-69°) benzylideneazines respectively.

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