PREPARATION OF SUBSTITUTED THIIRANES AND ETHYLENES IN THE REACTION OF 3-PIPERIDINO-2-PHENYLIDENE-1-THIONE WITH MONO- AND DIPHENYLDIAZOMETHANES

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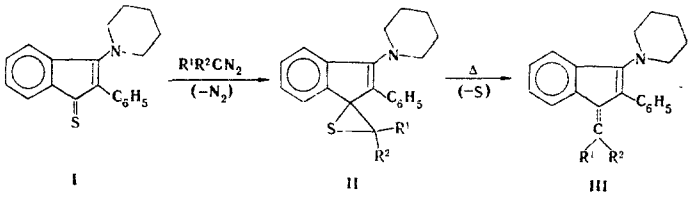
Both thiiranes and 1,3-dithiolanes are obtained in the reactions of thioketones with substituted diazomethanes [1]. β-Aminothiones of the indene series react with diazomethane to give the corresponding 1,3-dithiolanes [2]. We have observed that 3-piperidino-2-phenylidene-1-thione (I) reacts readily with diphenyldiazomethane at room temperature in benzene or ether solution to give good yields of the corresponding thiiranes (II). As is the case with many thiiranes [3], when II are heated even gently, elemental sulfur is split out, and II are converted to ethylene derivative IIIa.

Only the corresponding ethylene (IIIb) is obtained in the reaction of aminothione I with phenyldiazomethane in ether or benzene, inasmuch as intermediate thiirane IIb apparently very readily splits out a sulfur atom.



I II III

II–III a $R^1, R^2 = C_6H_5$; $R^1 = H$; $R^2 = C_6H_5$

EXPERIMENTAL

Spiro[(3-piperidino-2-phenylidene)-1,2']-3',3'-diphenylthiirane (IIa). This compound, with mp 115° (dec.), was obtained in 80% yield. Found: C 84.3; H 6.2; N 3.1; S 6.8%. $C_{33}H_{29}NS$. Calculated: C 84.1; H 6.2; N 3.0; S 6.8%.

1-Diphenylmethylene-2-phenyl-3-piperidinoindene (IIIa). This compound, with mp 165-167° (isopropyl alcohol), was obtained in 98% yield. Found: C 89.9; H 6.6; N 2.9%. $C_{33}H_{29}N$. Calculated: C 90.2; H 6.6; N 3.2%.

1-Benzylidene-2-phenyl-3-piperidinoindene (IIIb). This compound, with mp 150-152°, was obtained in 64% yield. Found: C 89.5; H 7.1; N 3.4%. $C_{27}H_{25}N$. Calculated: C 89.3, H 6.9; N 3.9%. The structures of the compounds obtained in this study were confirmed by the IR and PMR spectra.

LITERATURE CITED

1. A. Schönberg, B. König, and E. Singer, Chem. Ber., 100, 767 (1967).
2. N. A. Korchevin, V. A. Usev, and M. G. Voronkov, Khim. Geterotsikl. Soedin., 713 (1974).
3. A. Schönberg and R. Ardenne, Chem. Ber., 101, 346 (1968).

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