

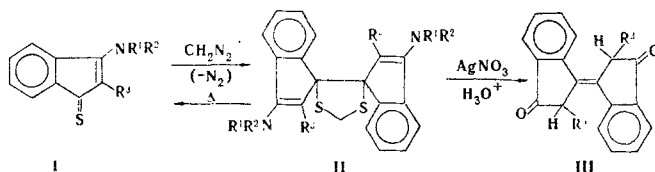
FORMATION OF SUBSTITUTED 1,3-DITHIOLANES IN
REACTIONS OF 3-AMINO-2-ARYLIDENE-1-THIONES
WITH DIAZOMETHANE

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N,N-Disubstituted 3-amino-2-arylidene-1-thiones (I), which are vinylogs of thioamides, react readily with diazomethane in ether solution at room temperature to give substituted 1,3-dithiolanes (II). A similar reaction path is observed only for thioketones [1] and is unknown for thioamides [2].

When the 1,3-dithiolanes obtained (II) are refluxed in high-boiling solvents, they are, as usual [3], cleaved into two products, one of which is the starting aminothione (I). When II is treated with an aqueous alcohol solution of silver nitrate, the dithiolane ring is cleaved with simultaneous hydrolysis of the amino groups in the II molecules to give the corresponding 3,3'-dioxo-2,2'-diaryldiindanylidenes (III). Cleavage of 1,3-dithiolanes under such conditions has not been described in the literature.



I-III a $R^1, R^2 = (CH_2)_5$, $R^3 = C_6H_5$; b $R^1, R^2 = (CH_2)_5$, $R^3 = p-CH_3OC_6H_4$; c $R^1, R^2 = CH_3$, $R^3 = C_6H_5$

EXPERIMENTAL

Dispiro[bis(3-piperidino-2-phenylidene)-4,1':5.1']-1,3-dithiolane (IIa). This compound, with mp 160° (dec., benzene-methanol) was obtained in 90% yield. Found: C 78.9; H 6.4; N 4.6; S 10.2%. $C_{41}H_{40}N_2S_2$. Calculated: C 78.8; H 6.4; N 4.5; S 10.3%; M 622.

Dispiro[bis(3-piperidino-2-(p-methoxyphenylidene)-4,1':5.1')-1,3-dithiolane (IIb). This compound, with mp 135° (dec.), was obtained in 81% yield. Found: C 75.6; H 6.3; N 3.9; S 9.4%. $C_{43}H_{44}N_2O_2S_2$. Calculated: C 75.4; H 6.4; N 4.1; S 9.4%.

Dispiro[bis(3-dimethylamino-2-phenylidene)-4,1':5.1']-1,3-dithiolane (IIc). This compound, with mp 120° (dec.), was obtained in 70% yield. Found: C 77.2; H 6.0; S 11.8%. $C_{35}H_{32}N_2S_2$. Calculated: C 77.2; H 5.9; S 11.8%. IR spectrum (in KBr), cm^{-1} : 1495, 1610 (aromatic ring C=C), 1580 (C=C in a five-membered ring). PMR spectrum (in $CDCl_3$ with tetramethylsilane as the standard): τ 5.69 ppm.

3,3'-Dioxo-2,2'-diphenyldiindanylidene (IIIa). This compound, with mp $237-238^\circ$ (benzene-hexane), was obtained in 99% yield. Found: C 87.1; H 4.6%. $C_{30}H_{20}O_2$. Calculated: C 87.4; H 4.8%.

3,3'-Dioxo-2,2'-di(p-methoxyphenyl)diindanylidene (IIIb). This compound, with mp $219-220^\circ$, was obtained in 92% yield. Found: C 81.6; H 4.9%. $C_{32}H_{24}O_4$. Calculated: C 81.4, H 5.1%. Intense bands at 1708 cm^{-1} (C=O) are present in the IR spectra of diketones III.

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