

CCA-914

YU ISSN 0011-1643

547.398.4

Note

Thioamides. XIII^a. The Preparation of Some Substituted Bisthioamides^b

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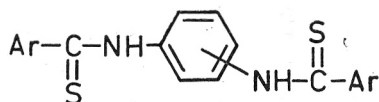
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Received March 21, 1975

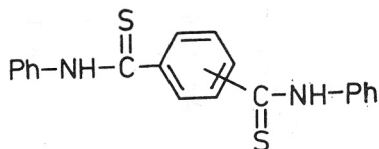
As a part of our studies on orientation in oxidative cyclization of *N*-arylthioamides, we turn the attention to oxidations of bisthioamides derived from isomeric phenylenediamines or isomeric benzenedicarboxylic acids¹. Among numerous substituted thioamides synthesized as yet² there are not many examples either of *N,N'*-bis(thioaroyl)phenylenediamines (I), or of benzenebis(carbothioanilides) (II).

In this paper we wish to report the preparation of such thioamides (Table I and II).



Ar = phenyl or 2-furyl

I



II

All thioamides described in this paper were synthesized by thionation of the corresponding, mostly known, amides with phosphorus pentasulfide². It should be pointed out that we were unable to convert *N,N'*-dibenzoyl-*o*-phenylenediamine and *N,N'*-diphenylphthalidamide to the corresponding bisthioamides, while the conversion of *N,N'*-di(2-furoyl)-*o*-phenylenediamine was successful. One could presumably find an explanation in steric effects.

The ir spectra of the prepared bisthioamides (similarly as those of other secondary thioamides) show B, C, D, F and G bands³. For the identification purposes the very strong or strong bands at 1537—1515 cm^{-1} ($\delta_{\text{NH}/\nu_{\text{CN}}}$), 1358—1330 cm^{-1} ($\nu_{\text{CN}}/\delta_{\text{NH}}$) and 1052—985 (ν_{CS}) were most useful^{4,5}.

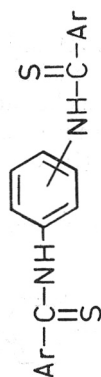
^a Part XII: K. Jakopčić and B. Karaman, *Bull. Sci. Conseil. Acad. Yougosl.* **18** (1973) 65.

^b Taken in part from the *Ph. D. Thesis* of D. Petrova, University of Zagreb, 1973.

^c Correspondance should be addressed to K. Jakopčić.

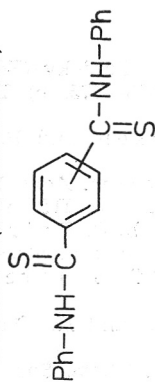
TABLE I

N,N'-Bis(thioaroyl)phenylenediamines



No.	Ar	Isomer	Starting compound M. p. °C	React. time (hrs)	Yield %	M. p. °C	Formula	Mol. wt.	Anal.		ir spectrum ^d /cm ⁻¹		
									Calcd	Found			
										%C	%H	%N	
I	C ₆ H ₅	<i>m</i> -	237—9 ^a	1 ^h 15'	88	209—11°	C ₂₀ H ₁₆ N ₂ S ₂	348.4	68.93	4.63	8.04	3160s, 1535s/1510vs, 1350vs, 1017s	
II	C ₆ H ₅	<i>p</i> - ^c	334—6 ^b	4	59	267—9°	C ₂₀ H ₁₆ N ₂ S ₂	348.4	68.93	4.63	8.04	3170s, 1537vs, 1350vs, 990s	
III	C ₄ H ₃ O	<i>o</i> -	216—8	2	50	180—2°	C ₁₆ H ₁₂ N ₂ O ₂ S ₂	328.4	69.09	4.60	7.93	3170s, 1515vs, 1340vs, 1025vs, 985vs	
IV	C ₄ H ₃ O	<i>m</i> -	196—7	1	69	149—50°	C ₁₆ H ₁₂ N ₂ O ₂ S ₂	328.4	58.52	3.63	8.53	3215/3190s, 1520vs, 1330vs, 1025vs, 980vs	
V	C ₄ H ₃ O	<i>p</i> -	270—1	2	46	221—3°	C ₁₆ H ₁₂ N ₂ O ₂ S ₂	328.4	58.37	3.47	8.33	3215s, 1520vs, 1350vs, 1020vs, 980vs	
										58.24	3.81	8.27	
										58.52	3.63	8.53	
										58.23	3.38	8.72	

TABLE II
Benzenebis(carbothionilides)



No.	Isomer	Starting compound M. p. °C	React. time (hrs)	Yield %	M. p. °C	Formula	Mol. wt.	Anal.		ir spectrum ^e cm ⁻¹	
								Calcd	Found		
								%C	%H	%N	
VI	<i>m</i> -	279—81 ^a	1 ^h 15'	59	242—4 ^c	C ₂₀ H ₁₆ N ₂ S ₂	348.4	68.93	4.63	8.04	3160s, 1534vs, 1358vs, 1052s
VII	<i>p</i> -	333—6 ^b	1 ^h 15'	79	280—2 ^d	C ₂₀ H ₁₆ N ₂ S ₂	348.4	68.03	4.44	7.86	3170s, 1530vs, 1335vs, 985s

^a Lit⁸ 280 °C; ^b lit⁹ 334—7 °C; ^c recr. from HOAC; ^d recr. from EtOH; ^e frequencies of characteristic bands.

EXPERIMENTAL

Melting points are uncorrected.

IR Spectra were taken on Perkin-Elmer Model 521 spectrophotometer in KBr pellets. Diamides except difuroylphenylenediamines were known, and were prepared according to procedure of Adams and Anderson⁶ from corresponding acylchloride and amine in pyridine.

The Preparation of Bisthioamides I—VII

Phosphorus pentasulfide (2 moles pro mole of amide) was added to the hot solution or suspension of the diamide in dry dioxane*.

The reaction mixture was heated near the boiling point of the solvent. After the reaction was over, the mixture was poured into 5—10 volumes of water. The oily product soon crystallized. The product was dissolved in warm (below 50 °C) 10% aqueous sodium hydroxide and the filtered solution carefully neutralized with 10% hydrochloric acid. The product was recrystallized from hot glacial acetic acid or ethanol.

Acknowledgements. We are deeply indebted to late Prof. V. Hahn for suggesting the problem. The authors wish to thank Prof. I. Petrov for the discussion of IR spectra, and Mrs. I. Guštak-Mašek for the microanalyses.

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SAŽETAK

Tioamidi. XIII. Priprava nekih supstituiranih bistioamida

D. Petrova i K. Jakopčić

Do sad neopisani *N,N'*-bis(tioaroil)fenilendiamini i benzenbis(karbotioanilidi) pripravljeni su reakcijom odgovarajućih amida s fosforpentasulfidom u suhom dioksanu ili piridinu. Bistioamidi (Tabela I i II) pripravljeni su sa svrhom istraživanja njihove oksidativne ciklizacije, a karakterizirani su infracrvenim spektrima i elementarnom analizom.

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prispjelo 21. ožujka 1975.

* Except II when dry pyridine was used.