

[CONTRIBUTION FROM THE SCHOOL OF PHARMACY AND THE MORLEY CHEMICAL LABORATORY OF WESTERN RESERVE UNIVERSITY]

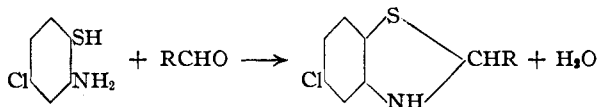
THE CONDENSATION OF ALDEHYDES AND KETONES WITH ORTHO-AMINOTHIOPHENOLS, BENZOTHAZOLINES AND BENZOTHAZOLES. II

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RECEIVED SEPTEMBER 28, 1931

PUBLISHED JANUARY 7, 1932

In a previous paper¹ it was shown that aldehydes condense with 2-amino-4-chlorothiophenol to give benzothiazolines.



A number of benzothiazolines were described in which the radical R was both aliphatic and aromatic. These substances were shown to be very easily oxidized to the corresponding benzothiazole, especially if R is an aromatic radical.

In the present work this reaction has been further studied to include the more common aliphatic aldehydes through valeraldehyde as well as several derivatives of benzaldehyde. With aliphatic aldehydes only benzothiazolines were obtained as the condensation products; the aromatic aldehydes employed, however, unlike the previous cases studied, gave only benzothiazoles under the same conditions.²

α -Unsaturated aldehydes gave only resinous products although a number of condensing agents were used. In one case, cinnamic aldehyde, the benzothiazole was separated in small yield.

The derivatives of aliphatic and aromatic aldehydes are easily obtained as pure crystalline solids. Since the reagent 2-amino-4-chlorothiophenol is easily prepared, these derivatives may be conveniently used for the identification of aldehydes.

Previous attempts to condense *o*-aminothiophenol with ketones have been unsuccessful.³

By using the method employed with aldehydes and prolonging the reaction time, we were able to obtain benzothiazolines from certain ketones. The spiro compounds obtained from cyclopentanone and cyclohexanone are highly colored, amethyst and dark blue, respectively.

Experimental

Preparation of Benzothiazolines and Benzothiazoles.—The method employed was the same as that used in previous work. One mole of 2-

¹ Lankelma and Sharnoff, *THIS JOURNAL*, 53, 2654 (1931).

² Evidence has previously been presented to show that this failure to obtain benzothiazolines is due to oxidation in the process of purification.¹

³ Bogert and Stull, *THIS JOURNAL*, 47, 3078 (1925).

TABLE I

PROPERTIES AND ANALYTICAL DATA OF ALDEHYDE AND KETONE DERIVATIVES

Aldehyde or ketone	Product Benzothiazoline	M. P., °C.	Formula	Carbon, %		Hydrogen, %		Chlorine, %		
				Calcd.	Found	Calcd.	Found	Calcd.	Found	
Butyric	2-Propyl-5-chloro- ^a	49	C ₁₀ H ₁₂ NCIS	56.15	56.17	5.67	5.57			
Isobutyric	2-Isopropyl-5-chloro- ^a	45	C ₁₀ H ₁₂ NCIS	56.15	56.48	5.67	5.53			
Valeric	2-Butyl-5-chloro- ^a	78	C ₁₁ H ₁₄ NCIS	57.97	58.21	6.21	6.14			
Isovaleric	2-Isobutyl-5-chloro- ^a	69	C ₁₁ H ₁₄ NCIS	57.97	58.04	6.21	6.32			
Phenylacetic	2-Benzyl-5-chloro- ^a	89	C ₁₄ H ₁₂ NCIS	64.20	64.54	4.62	4.62			
	Benzothiazole									
Furfural	2-Furyl-5-chloro- ^a	122	C ₁₁ H ₆ ONCIS	56.00	56.15	2.56	2.78			
<i>m</i> -Nitrobenz-	2-(3'-Nitrophenyl)-5-chloro- ^b	146	C ₁₃ H ₇ O ₂ N ₂ CIS	53.65	53.90	2.43	2.54			
Salicylic	2-(2'-Hydroxyphenyl)-5-chloro- ^c	201	C ₁₃ H ₈ ONCIS	59.63	59.78	3.08	3.22	13.56	13.80	
Vanillin	2-(3'-Methoxy-4'-hydroxyphenyl)-5-chloro- ^d	173	C ₁₄ H ₁₀ O ₂ NCIS	57.59	57.48	3.45	3.67	12.16	12.37	
Piperonal	2-(3',4'-Methylenedioxyphenyl)-5-chloro- ^d	173	C ₁₄ H ₈ O ₂ NCIS	57.99	57.75	2.78	2.88	12.24	12.22	
Cinnamic	2-Styryl-5-chloro- ^a	134	C ₁₆ H ₁₀ NCIS	66.25	66.52	3.71	3.63	13.05	13.04	
	Benzothiazoline									
Acetone	2,2-Dimethyl-5-chloro- ^a	37	C ₉ H ₁₀ NCIS	54.08	53.72	5.05	5.11	17.80	18.07	
Acetophenone	2-Methyl-2-phenyl-5-chloro- ^a	71	C ₁₄ H ₁₂ NCIS	64.20	64.03	4.62	4.57	13.55	13.69	
Cyclohexanone	5'-Chloro-spiro-(1-cyclohexane-2') ^a	93	C ₁₂ H ₁₄ NCIS	60.07	59.73	5.93	5.97	14.82	14.82	
Cyclopentanone	5'-Chloro-spiro-(1-cyclopentane-2') ^a	47	C ₁₁ H ₁₂ NCIS	58.48	58.31	5.32	5.23			

^a Solvent, alcohol. ^b Butyl alcohol. ^c Xylene. ^d Propylene glycol.

amino-4-chlorothiophenol hydrochloride was dissolved in pyridine and one mole of the aldehyde or ketone was added dropwise to the warm solution. The mixture was finally heated on the water-bath. A few minutes to a half hour of heating sufficed for the aldehydes; the ketones required from one to six hours. The condensation product was precipitated by acidifying the cold solution.

Summary

1. Aliphatic aldehydes condense with 2-amino-4-chlorothiophenol to give benzothiazolines; aromatic aldehydes may give a benzothiazoline or a benzothiazole, depending upon the aldehyde employed.
2. Certain ketones condense with 2-amino-4-chlorothiophenol to give benzothiazolines.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT AT THE OHIO STATE UNIVERSITY]
**NATURAL AND SYNTHETIC RUBBER. VIII. PRODUCTS OF THE
DESTRUCTIVE DISTILLATION OF SODIUM RUBBER**

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RECEIVED SEPTEMBER 30, 1931

PUBLISHED JANUARY 7, 1932

In the first paper¹ of this series it was shown that the pyrolysis products of natural rubber are directly related to the rubber molecule. The pyrolysis products of sodium rubber should bear a similar relationship to its molecular structure, and the difference between its formula and that of natural rubber should be detected by a study of these products.

Four kilograms of sodium rubber was destructively distilled. The resulting hydrocarbons were separated by fractional distillation, and identified by the methods previously employed.¹ The results are summarized in Table I. The starred compounds were identified by methods described in the experimental part. The components marked "abridged" were noted during the course of the fractionation, but were not investigated more fully due to the limited amount of available material.

The sodium rubber used was benzene free. Hence the presence of benzene among the distillation products confirms the viewpoint of its origin as expressed in paper I.

m-Xylene is not the only xylene formed. This agrees with the expectations based on the structure of sodium rubber indicated in a previous paper.² Mass action considerations predict the ratio of ortho:meta:para-xylene as 5:10:5, but actually it is found to be <1:10:2. The reduction of the *o*-isomer can be explained by the assumption made in paper I that free valences on secondary or tertiary carbon atoms will accept hydro-

¹ Midgley and Henne, *THIS JOURNAL*, **51**, 1215-1226 (1929).

² Ref. 1, pp. 1294-1296.