Summary

Consideration of the kinetic results on the decomposition of ethylene diiodide shows that a chain mechanism explains them completely. A similar conclusion is reached for the decomposition of allyl alcohol diiodide, and the photo-addition of bromine to cinnamic acid.

The proposal is made that the addition of halogens to an ethylenic linkage, or the corresponding reverse reaction need never occur in a single act.

STANFORD UNIVERSITY, CALIF.

RECEIVED JANUARY 27, 1936

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

The Saponification and Thermal Decomposition of Mixed Diacyl Derivatives of 2-Amino-4-chlorothiophenol

BY HERMAN P. LANKELMA AND EDWARD VOPICKA

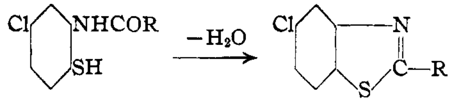
A study of mixed acyl derivatives of an *o*-aminophenol has shown that a migration of acyl between oxygen and nitrogen upon acylation, leading to identical mixed diacyl derivatives regardless of the order of introduction of the acyl radicals, is a general reaction. The acyl pair benzoyl–acetyl, for example, yield typical results in this respect.[1]

In a previous paper Lankelma and Knauf[2] have shown that when this acyl pair is employed with an *o*-aminothiophenol no migration of acyl occurred upon acylation, that is, an isomeric pair of mixed diacyl derivatives was obtained. Upon saponification of these mixed diacyl derivatives, however, the same monoacyl derivative, N-benzoyl, was obtained, showing that a migration of acyl between sulfur and nitrogen did occur upon saponification. The base employed in this work was 2-amino-4-chlorothiophenol.

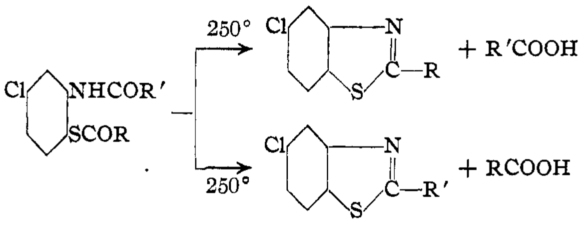
The present work, employing the same base, was undertaken to determine whether the behavior observed with the acyl pair benzoyl–acetyl was general where other pairs of acyl radicals were concerned. For this purpose the following four pairs of acyl radicals were employed: acetyl–phenylacetyl, acetyl–cinnamyl, benzoyl–cinnamyl, and benzoyl–phenylacetyl. Attempts to employ the propionyl radical were unsuccessful owing to the ease with which the mono-N-propionyl derivative lost water to form the corresponding benzothiazole.

It was found that with each of these four pairs of acyl radicals two isomeric diacyl derivatives were obtained, depending upon the order in which the acyl radicals were introduced. Also in each case saponification of the isomeric mixed diacyl derivatives gave the same mono-N-acyl derivative. Because of the ease with which these monoacyl derivative lose water to form the corresponding benzothiazole they are often difficult to purify.[2]

For this reason they were identified in this work in the form of the corresponding benzothiazoles.



It was also found that upon heating to a temperature of about 250° the diacyl derivatives were smoothly decomposed into the benzothiazole and the acid. In case a mixed diacyl derivative is subjected to this thermal decomposition it could yield two sets of products, depending upon the course of the cleavage.



Five isomeric pairs of mixed diacyl derivatives were decomposed in this way and in each case the pair in question gave a single set of products. The course of this cleavage therefore appears to be determined by the nature of the acyl radicals involved rather than by the element, sulfur or nitrogen, to which they are attached. It was also found that the benzothiazole obtained from a given isomeric pair of mixed diacyl derivatives by thermal decomposition was the same as that obtained by saponification at room temperature.

---

[1] See papers by Raiford, THIS JOURNAL (1919–1926).

[2] Lankelma and Knauf, *ibid.*, **53**, 309 (1931).

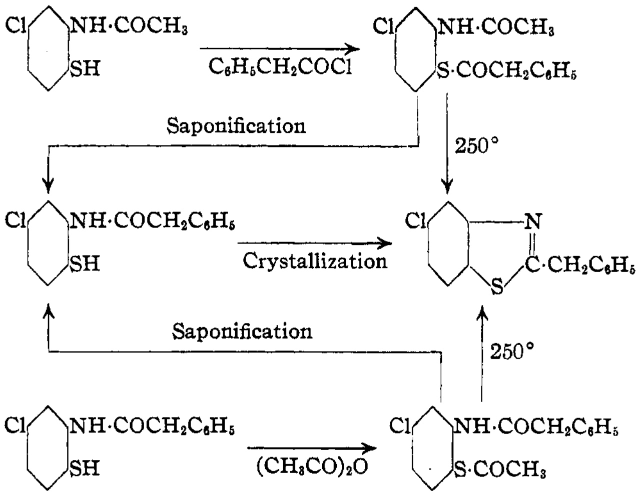
TABLE I

Acyl derivative	M. p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
2-Cinnamylamino-4-chlorothiophenol	153–155	$C_{15}H_{12}ClNOS$	62.15	62.14	4.18	4.17
2-Phenylacetylamino-4-chlorothiophenol	126	$C_{14}H_{12}ClNOS$	60.51	60.48	4.36	4.35
2-Cinnamylamino-4-chlorophenyl thiocinnamate	172–173	$C_{24}H_{18}ClNO_2S$	68.63	68.74	4.32	4.35
			Chlorine, %		Sulfur, %	
2-Phenylacetylamino-4-chlorophenyl thiophenylacetate	149	$C_{22}H_{18}ClNO_2S$	8.96	9.02	8.10	8.16

TABLE II

Mixed diacyl derivative	M. p., °C.	Formula	Chlorine, % Calcd.	Chlorine, % Found	Sulfur, % Calcd.	Sulfur, % Found
2-Acetylamino-4-chlorophenyl thiocinnamate	142	$C_{17}H_{14}ClNO_2S$	10.70	10.65	9.67	9.61
2-Acetylamino-4-chlorophenyl thiophenylacetate	149	$C_{16}H_{14}ClNO_2S$	11.09	11.10	10.03	9.96
2-Benzoylamino-4-chlorophenyl thiocinnamate	122	$C_{22}H_{16}ClNO_2S$	9.01	8.92	8.14	8.09
2-Benzoylamino-4-chlorophenyl thiophenylacetate	154	$C_{21}H_{16}ClNO_2S$	9.29	9.26	8.40	8.37
			Carbon, %		Hydrogen, %	
2-Cinnamylamino-4-chlorophenyl thioacetate	138	$C_{17}H_{14}ClNO_2S$	61.51	61.51	4.26	4.23
2-Phenylacetylamino-4-chlorophenyl thioacetate	122–123	$C_{16}H_{14}ClNO_2S$	60.07	60.00	4.41	4.40
2-Cinnamylamino-4-chlorophenyl thiobenzoate	164–165	$C_{22}H_{16}ClNO_2S$	67.06	67.01	4.10	4.05
2-Phenylacetylamino-4-chlorophenyl thiobenzoate	161	$C_{21}H_{16}ClNO_2S$	66.03	65.71	4.23	4.20

The following formulation of the results obtained employing the acyl pair acetyl–phenylacetyl will serve to illustrate the results obtained with the other pairs of acyl radicals employed.



Upon saponification and thermal decomposition of the following five isomeric pairs of mixed diacyl derivatives, the acyl residue shown in italics is found in the benzothiazole: *phenylacetyl*–acetyl, *cinnamyl*–acetyl, *benzoyl*–phenylacetyl, *cinnamyl*–benzoyl, *benzoyl*–acetyl.

Experimental

Preparation of Mixed Diacyl Derivatives of 2-Amino-4-chlorothiophenol.—The mixed diacyl derivatives were prepared from 2-amino-4-chlorothiophenol by the procedure described by Lankelma and Knauf.[2] This involves acylating the 2-amino-4-chlorothiophenol to the diacyl derivative, saponifying to obtain the N-monoacyl derivative, and acylating this to give the mixed diacyl derivative. Table I is a summary of the diacyl and monoacyl derivatives employed as intermediates, and Table II describes the mixed diacyl derivatives obtained.

Saponification of the Mixed Diacyl Derivatives.—The mixed diacyl derivative was allowed to stand at room temperature with potassium hydroxide in alcohol. The resulting solution was then diluted with about five parts of water, acidified and the precipitate of monoacyl derivative filtered by suction. The monoacyl derivative was then crystallized from alcohol, whereby it was converted into the corresponding benothiazole.

Thermal Decomposition of the Mixed Diacyl Derivatives.—The mixed diacyl derivative was heated in a sealed glass ampoule to 250° in a bath of diphenyl oxide for about an hour. The resulting mixture was treated with dilute sodium hydroxide to remove the acid present and the residue of benzothiazole was purified by crystallization from alcohol. Of the three benzothiazoles obtained, two have been described in the literature; the third is described herewith.

2-BENZYL-5-CHLOROBENZOTHIAZOLE

		Calcd.	Found
Melting point, °C.	81–82		
Formula	$C_{14}H_{11}ClNS$		
Carbon, %		64.46	64.44
Hydrogen, %		4.25	4.25

Summary

1. Four isomeric pairs of mixed diacyl derivatives of 2-amino-4-chlorothiophenol were prepared. No migration of acyl occurred upon acylation.

2. Saponification of the isomers of a given pair of mixed diacyl derivatives gave but one monoacyl compound, and each pair behaved in this

way. A migration of acyl between sulfur and nitrogen occurred upon saponification.

3. Each of these isomeric pairs of mixed diacyl derivatives upon thermal decomposition at 250° yields a single benzothiazole. In each case this benzothiazole is the same as that obtained upon saponification at room temperature.

CLEVELAND, OHIO RECEIVED JANUARY 22, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Reaction of Allyl Bromide with Acetylenic Grignard Reagents[1]

BY JAMES P. DANEHY, D. B. KILLIAN AND J. A. NIEUWLAND

The reaction of allyl bromide with Grignard reagents was first reported by Tiffeneau[2] and has been used by numerous investigators[3] for the synthesis of hydrocarbons containing an olefinic linkage at a terminal carbon atom.

Grignard and his co-workers[4] have described allyl, *n*-amyl allyl and phenylallylacetylenes prepared from the corresponding acetylenic Grignard reagent and allyl bromide. In a subsequent publication, Grignard[5] has reported that the preparation of allylacetylene from allyl bromide and monomagnesium acetylene bromide could not be repeated since the monomagnesium bromide of acetylene apparently was not formed as previously observed. However, no such difficulty occurred in the preparation of the Grignard reagent of an alkylacetylene or in the preparation of the corresponding allylacetylene.

Using the usual Grignard technique, attempts in these laboratories to synthesize alkyl allyl and aryl allyl acetylenes have failed without exception. For example, when allyl bromide was added to an ethereal solution of *n*-butylacetylenemagnesium bromide, no reaction was observed. After standing for twenty-three days at room temperature with frequent agitation, part of the mixture was hydrolyzed and fractionated and yielded only allyl bromide and *n*-butylacetylene. A small amount of cuprous chloride was added to the remainder of the mixture. A vigorous, rapid reaction ensued, and the mixture separated into two layers. Fractionation of the upper layer without hydrolysis yielded *n*-butylallylacetylene. The lower layer was poured into a dilute acid–ice mixture, dried and fractionated whereupon a small additional amount of *n*-butylallylacetylene was obtained.

In another experiment, anhydrous acetone was added to the mixture of *n*-butylacetylenemagnesium bromide and allyl bromide. Upon hydrolysis and fractionation, the original quantity of allyl bromide was recovered and 1,1-dimethyl-2-heptyn-1-ol,[6] not previously prepared, was obtained in high yield, indicating that the *n*-butylacetylenemagnesium bromide originally present had not reacted with the allyl bromide.

Refluxing an alkylacetylene Grignard reagent and allyl bromide in benzene or di-*n*-amyl ether for periods varying from two to twelve hours did not effect reaction. Using cuprous chloride, the appropriate alkyl or arylacetylene Grignard reagent in ethereal solution and allyl bromide, *n*-amyl, *n*-butyl, phenyl and vinyl allylacetylenes have been prepared and described. The physical constants of these compounds are reported in the table.

In general, these reactions seem to be catalyzed by both cuprous and cupric halides and cuprous cyanide. Cuprous bromide and cuprous chloride produce the highest yields of the substituted allylacetylenes. Copper bronze, cuprous and cupric sulfide apparently do not catalyze these reactions.

The pronounced effect of impurities in the magnesium on the course of the reaction of the Grignard reagents has been noted frequently.[7] This might account, at least in part, for the different results obtained in these laboratories and abroad.

---

(1) Ninth paper on the alkylacetylenes and their addition compounds; previous paper, *J. Org. Chem.*, **1**, in press (1936).

(2) Tiffeneau, *Bull. soc. chim.*, [3] **29**, 1156 (1903); *Compt. rend.*, **139**, 481 (1904).

(3) For numerous references see Mulliken, *et al.*, THIS JOURNAL, **57**, 1605 (1935).

(4) Grignard and Lapayre, *Bull. soc. chim.*, [4] **43**, 141 (1928); Grignard, Lapayre and Tcheoufaki, *Compt. rend.*, **187**, 517 (1928).

(5) Grignard and Lapayre, *ibid.*, **192**, 250 (1931).

(6) B. p. 92–93° (33 mm.); n^{19}_{D} 1.4479; d^{19} 0.855; MR_D: calcd. 43.29; found 43.87. *Anal.* Calcd. for $C_9H_{16}O$: C, 77.14; H, 11.52. Found: C, 76.40; H, 12.00.

(7) Gilman, *et al.*, *Rec. trav. chim.*, **54**, 584 (1935); Cusa and Kipping, *J. Soc. Chem. Ind.*, **53**, 213–214T (1934); Job, Reich and Dubien, *Bull. soc. chim.*, [4] **37**, 976 (1925); Job and Dubien, *ibid.*, [4] **39**, 583 (1926).