decreases during formation at 25° are plotted as functions of the number of the carbon atoms in the acid radicals. Both curves show the sawtooth pattern which is a characteristic representation of many of the properties of fatty acids.

The acid radicals which contain two and four carbon atoms use less of the total affinity of the metals than do the acid radicals which contain three and five carbon atoms, and the corresponding complexes hold their pyridine more firmly, having lower dissociation pressures, their formation being accompanied by greater shrinkages.

Except for the effect of odd and even numbers of carbon atoms, the general effect of increasing the number of carbon atoms in the acid radical appears to be to reduce the residual affinities of the metal atoms and to leave less available for combination with pyridine.

The effect of a fork in the carbon chain is small.

The nickel atom has greater chemical forces available for coördinative combination with pyridine at 25° than has the cobalt atom, for the nickelous complex salts are formed with greater volume decreases, and have lower dissociation pressures, than the cobaltous compounds.

Summary

The dissociation pressures of cobaltous and nickelous dipyridine acetate, propionate, butyrate, isobutyrate, and valerate have been determined over the temperature range from 15–20° to 85–90°.

The densities at 25° of the complexes and of their component salts have been determined, and the volume changes which occur at 25° during the combination of the simple salts with pyridine have been calculated. The complexes of which the formation is accompanied by the greater shrinkages have the lower dissociation pressures.

The effect of groups upon the residual affinities of the metal atoms is discussed.

CAMBRIDGE, MASS. RECEIVED MARCH 5, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE CITY COLLEGE, THE COLLEGE OF THE CITY OF NEW YORK]

Alkanolamines. IX. Reducing and Hydrolyzing Action of the Ethanolamines on the Dichloronitrobenzenes

BY CHESTER B. KREMER AND AARON BENDICH

In a preceding article of this series,[1] an account was given of the reactions occurring between the isomeric dichloronitrobenzenes and monoethanolamine as carried out in neutral solvents. When these reactions are carried out in the absence of neutral solvents, the course followed is quite different, the condensing ability of the amino alcohol is considerably decreased and there is substituted the tendency toward reduction, hydrolysis and the formation of addition compounds. The finding of a combination of these tendencies, together with condensation, in a single run, is not infrequent. Insofar as the reductions involved, not only are the starting materials reduced to various stages, but there is also noted the reduction of an expected end-product. Under certain circumstances, it is found that when a dichloronitrobenzene is treated with monoethanolamine in the presence of anhydrous sodium carbonate, there can be isolated from the reaction mixture: (1) the condensation product, (2) a reduced product of the dichloronitrobenzene, either the azo or amino derivative, (3) the reduced condensation product, (4) an hydrolysis product of the dichloronitrobenzene, and in some cases (5) addition compounds of the type $xC_6H_3NO_2Cl_2 \cdot yNH_2CH_2CH_2OH$ where x and y are usually 1 or 2.

In order to make this survey more complete, the action of diethanolamine and triethanolamine upon the isomeric dichloronitrobenzenes was also studied. The ability of these ethanolamines to reduce, hydrolyze and form addition products with the isomers is, in most cases, greater than that of monoethanolamine. While condensations are possible in the case of diethanolamine, there was no instance of such reaction during the course of this work. Condensations involving this amino alcohol do occur when the reaction takes place in a neutral solvent; but even here the tendency is not great.

The fact that good yields of amino products can be obtained in these reactions is of interest since mononitro compounds are not generally re-

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[1] Kremer and Bendich, THIS JOURNAL, 61, 2658 (1939).

duced to this stage in alkaline media. In this research, the reductions yielded only azo or amino compounds as final products, usually a mixture of the two. In only one or two instances was there any indication of the azoxy state and in no case were hydrazo compounds indicated.

Of the possible azo compounds derived by reduction of the dichloronitrobenzenes, only the 2,2′,5,5′-tetrachloroazobenzene is reported in the literature. This article reports the formation of two others, namely, 3,3′,4,4′-tetrachloroazobenzene and 3,3′,5,5′-tetrachloroazobenzene. It was not possible to isolate the azo compounds of the other isomers, tars being the main products in these cases. The presence of the azoxy state was suspected in several instances, but no satisfactory isolation was effected. The azo compounds obtained were orange solids, recrystallizable from benzene or petroleum ether–benzene mixtures.

Experimental

The isomeric dichloronitrobenzenes were prepared as previously described.[1] The ethanolamines were obtained from the Union Carbide and Carbon Corporation.

The experimental procedure followed in the major portion of this work can be summarized as follows. The apparatus used was a three-necked, round-bottom flask equipped with mechanical stirrer, reflux condenser and dropping funnel. The dichloronitrobenzene was introduced into the flask, along with any added alkali, and the whole gently warmed until the dichloronitrobenzene was melted. The ethanolamine was then added dropwise and the mixture refluxed for several hours. After refluxing, the reaction mixture was steam distilled until the distillate was clear. The latter was then freed of any solid or oil materials and extracted with ethyl ether and the ether extracts dried over anhydrous magnesium sulfate. The aqueous layers were made acid with hydrochloric acid and extracted with ethyl ether and these extracts were likewise dried.

The residue in the steam distillation flask was filtered from any resulting solid and alkaline and acid ether extracts made of the filtrate following the procedure described above.

The various extracts and residues were then systematically investigated and the results are summarized in Table I. All reactants are expressed in molar ratios although the actual amounts involved were usually fractions of those indicated.

Preparation of Azo Compounds. 3,3′,5,5′-Tetrachloroazobenzene.—In one run, monoethanolamine, 2,5-dichloronitrobenzene and anhydrous sodium carbonate in molar ratios were refluxed for approximately four hours. The reaction mixture was then subjected to steam distillation. 3,5-Dichloroaniline was detected in the steam distillate in a yield of about 20%. There remained in the distillation flask a very dark red solid which was filtered off. This was washed twice with hot alcohol and then recrystallized from benzene. The resulting product was orange in color and melted at 158.5° (cor.). Calculated % N for 3,3′,5,5′-tetrachloroazobenzene, 8.76; % N found, 8.88. The product was further identified by reduction with tin and hydrochloric acid. This yielded a white crystalline substance giving a primary amine test and melting at 51° (the melting point of 3,5-dichloroaniline). A mixed melt-

TABLE I

	Reactants: ratio of 1 mol 2,5-dichloronitrobenzene with	Hours refluxed	Products isolated	Yields, %
1.	2 mols M. E. A.[b] 0.5 mol Na_2CO_3 (anhyd.)	4	4-Chloro-2-nitrophenol 2-(4-Chloro-2-nitroanilino)-ethanol 2-(4-Chloro-2-aminoanilino)-ethanol 2,5-Dichloroaniline	1 85 2 5
2.	Same as in "1"	16	4-Chloro-2-nitrophenol 2-(4-Chloro-2-nitroanilino)-ethanol 2-(4-Chloro-2-aminoanilino)-ethanol 2,5-Dichloroaniline	2 65 2 15
3.	1.5 mols M. E. A. 0.25 mols Na_2CO_3 (anhyd.)	20	4-Chloro-2-nitrophenol 2-(4-Chloro-2-nitroanilino)-ethanol 2,2′,5,5′-Tetrachloroazobenzene 2,5-Dichloroaniline	5 10 5 10
4.	2 mols M. E. A. 2 mols $NaC_2H_3O_2$	12	2-(4-Chloro-2-nitroanilino)-ethanol 2,5-Dichloroaniline	65 10
5.	1 mol T. E. A.[c] 1 mol Na_2CO_3 (anhyd.)	5	4-Chloro-2-nitrophenol 2,5-Dichloroaniline	30 5
6.	1 mol D. E. A.[d] 1 mol Na_2CO_3 (anhyd.)	5	4-Chloro-2-nitrophenol 2,5-Dichloroaniline	20 5
7.	1 mol M. E. A.	4	2-(4-Chloro-2-nitroanilino)-ethanol	10
8.	1 mol D. E. A.	4	2,5-Dichloroaniline	20
9.	1 mol T. E. A.	4	2,5-Dichloroaniline	35
	Ratio of 1 mol 3,4-dichloronitrobenzene with			
1.	1 mol M. E. A. 1 mol Na_2CO_3 (anhyd.)	4	2-(2-Chloro-4-nitroanilino)-ethanol[a]	90
2.	1 mol D. E. A. 1 mol Na_2CO_3 (anhyd.)	4	2-Chloro-4-nitrophenol 3,4-Dichloroaniline	1 3
3.	1 mol T. E. A. 1 mol Na_2CO_3 (anhyd.)	4	2-Chloro-4-nitrophenol 3,4-Dichloroaniline	10 7
4.	2 mols M. E. A.	4	2-(2-Chloro-4-nitroanilino)-ethanol[a]	90
5.	2 mols D. E. A.	2	3,3′,4,4′-Tetrachloroazobenzene	70
6.	2 mols D. E. A.	4	2-Chloro-4-nitrophenol 3,4-Dichloroaniline	5 5
7.	2 mols T. E. A.	2	3,3′,4,4′-Tetrachloroazobenzene 3,4-Dichloroaniline	40 10
	Ratio of 1 mol 2,4-dichloronitrobenzene with			
1.	2 mols M. E. A.	2	Mainly tar formation	
2.	2 mols D. E. A.	2	2,4-Dichloroaniline Tar formation	1
	Ratio of 1 mol 3,5-dichloronitrobenzene with			
1.	1 mol M. E. A. 1 mol Na_2CO_3 (anhyd.)	4	3,3′,5,5′-Tetrachloroazobenzene 3,5-Dichloroaniline	60 20
2.	2 mols D. E. A.	4	3,3′,5,5′-Tetrachloroazobenzene	40

[a] Previously reported as 2-(6-chloro-4-nitroanilino)-ethanol. [b] Abbreviation for monoethanolamine. [c] Abbreviation for triethanolamine. [d] Abbreviation for diethanolamine.

ing point with a known sample of 3,5-dichloroaniline showed no deviation.

In another run, diethanolamine was employed without added alkali. No attempt was made here to identify other products than azo which was present in about 40% yield.

Preparation of 3,3′,4,4′-Tetrachloroazobenzene.—The 3,4-dichloronitrobenzene was, in most cases, refluxed with either di- or triethanolamine. The experimental procedure was the same as described above. The amount of 3,4-dichloroaniline recovered was small, usually under 10%. The azo product was recrystallized from a petroleum ether–benzene mixture giving a light orange product melting at 195.5° (cor.). Analyses indicated a persistent impurity, difficult to remove through successive recrystallizations: calculated % N for 3,3′,4,4′-tetrachloroazobenzene, 8.76; N found, 9.15, 9.07. Further identification was furnished by reducing the product with tin and hydrochloric acid. A white product giving a primary amine test and melting at 71° was obtained. A mixed melting point with a known sample of 3,4-dichloroaniline was unchanged.

Discussion

That reduction of the dichloronitrobenzenes occurs in definite stages is clearly borne out by some of the experiments. The one involving the action of diethanolamine on 3,4-dichloronitrobenzene is representative. When the two are refluxed together for a period of two hours, the only reduction product isolated is the azo compound; if heating is continued for four hours, no tetrachloroazobenzene can be identified, but reduction to the amino state is found to have taken place.

In previous work,[1] it was established that the 2,4-, 3,4- and 2,5-dichloronitrobenzenes were the most reactive of the isomers insofar as condensation reactions were concerned, while the 2,3- and 2,6- were much less reactive. When we examine the reducing tendency of the ethanolamines upon the various isomers, this general division still holds. The latter two compounds were much given to tar formation, from which tars little of interest could be extracted. For this reason most of the reported work dealt with the reactions of the 2,5-, 3,4- and 3,5-isomers, the 2,5- especially having been studied at length.

Hydrolysis of one of the chloro groups of 2,5- and 3,4-dichloronitrobenzenes was found to occur in certain of the reactions. That the chloro groups of these compounds are more active than the corresponding chloro groups of the other isomers already has been amply demonstrated.

Summary

1. Reduction to the amino and azo condition is found to occur when the isomeric dichloronitrobenzenes are reacted upon by the ethanolamines in the absence of a neutral solvent.

2. Condensation, hydrolysis and addition reactions are also found to occur.

3. Two new azo compounds, 3,3′,4,4′- and 3,3′,5,5′-tetrachloroazobenzene, are reported.

NEW YORK, N. Y.

RECEIVED MARCH 16, 1940

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Ketene Acetals. V. The Reaction of Ketene Diethylacetal with Various Compounds Containing an Active Hydrogen[1]

BY HARRY M. BARNES,[2] D. KUNDIGER AND S. M. MCELVAIN

In the fourth paper[3] of this series the unusual hetero-enoid system that is present in ketene diethylacetal was discussed, particularly as it affected the polymerization of the compound. It was to be expected that the reaction of a compound having such a strong nucleophilic center as does ketene acetal with other substances containing an active hydrogen would be of considerable interest. The present paper is a report of the results obtained from a study of the reactions of a variety of compounds, in which hydrogen is found attached to halogen, oxygen, carbon and nitrogen, with ketene acetal.

At the time that the preparation of ketene acetal was first reported,[4] the vigorous reaction of both water and ethyl alcohol with it was noted. These reactions produce ethyl acetate and ethyl orthoacetate, respectively. The formation of the former compound probably, and the latter obviously, involves addition across the carbon to carbon double bond of ketene acetal, thus

$$CH_2=C(OEt)_2 + HOEt \longrightarrow CH_3C(OEt)_3$$

Secondary alcohols (*i*-propyl and *s*-butyl) react similarly, but *t*-butyl alcohol does not appear to

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[1] This work was supported in part by grants from the Wisconsin Alumni Research Foundation.

[2] Wisconsin Alumni Research Foundation Scholar, 1935–1936.

[3] Johnson, Barnes and McElvain, THIS JOURNAL, **62**, 964 (1940).

[4] Beyerstedt and McElvain, *ibid.*, **58**, 529 (1936).