precipitate of pure bromobenzoic methyl ester in 98% yield (identified by mixed melting point with an authentic sample). The filtrate on acidification gave the characteristic color reaction of acetoacetic acid with ferric chloride.

γ-Bromophenyl-γ-methoxy-β-methyl-γ-butyrolactone (Cyclic β-(Bromobenzoylbutyric) Methyl Ester), V.—Is prepared in good yield by the zinc and glacial acetic acid reduction of β-bromobenzoylcrotonic methyl ester at refluxing temperature, or by heating the above enol ether IV in glacial acetic acid for ten minutes at refluxing temperature; purified by repeated recrystallization from ethanol; rhombic truncated prisms of m. p. 98° (corr.).

Anal. Calcd. for $C_{12}H_{11}O_3Br$: C, 50.50; H, 4.60; Br, 28.04. Found: C, 50.49; H, 4.41; Br, 28.47, 28.24.

It was hydrolyzed on heating for one to two minutes with an excess of alcoholic sodium hydroxide in almost quantitative yield to β-bromobenzoylbutyric acid (identified by mixed melting points). A solution of 1.2 g. of the cyclic ester in 10 cc. of methanol with 0.4 cc. of concd. sulfuric acid was refluxed for two hours. Upon diluting with ice water and sodium carbonate solution and extraction with ether, 1.1 g. of the oily open chain β-bromobenzoylbutyric methyl ester was isolated and identified by boiling point (190–192° at 18 mm.), refractive index, n_D^{28} 1.547 (the analytical sample prepared previously[1] showed n_D^{28} 1.549), and by hydrolysis to β-bromobenzoylbutyric acid.

Summary

The zinc–acetic acid reduction of cyclic β-bromobenzoylcrotonic methyl ester gives as the primary reduction product the enol methyl ether of β-(bromobenzoyl)-butyric acid, which is rearranged under suitable conditions first into the cyclic, then into the open chain β-bromobenzoylbutyric methyl ester. The mechanism of the reduction is regarded as a 1,6-addition of hydrogen to a conjugated system of the type O=C—C=C—C—O.

UNIVERSITY, VIRGINIA

RECEIVED MARCH 7, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA]

The Reaction of Chloroamines with Zinc Alkyls

BY GEORGE H. COLEMAN, H. P. ANDERSEN AND J. L. HERMANSON

Following the study of the reaction of monochloroamine[1] with Grignard reagents in which primary amines were formed, the work was extended to alkylchloroamines[2] with the thought of preparing secondary and tertiary amines. Both secondary and tertiary amines are formed by this reaction but the yields of secondary amines do not exceed 25% and the yields of tertiary amines are not above 10%. Tcherniak[3] reported the formation of triethylamine in the reaction of ethyldichloroamine with diethyl zinc.

The present work with zinc alkyls was undertaken for the purpose of comparing the yields of the various amines formed with those obtained with Grignard reagents as well as to determine the possibility of preparing tertiary amines in at least moderate yields.

When petroleum ether was used as a solvent in the reaction the yields of secondary amines were more than double those obtained with the corresponding Grignard reagents. In diethyl ether solution, however, the yields were of about the same order as those obtained with Grignard reagents.

For the preparation of tertiary amines the method has proven to be of no value. In none of the reactions with alkyldichloroamines was enough tertiary amine found to be identified. With dialkylchloroamines less than 2% of tertiary amine was formed.

Diethyl zinc was used in all but one reaction. The results with five chloroamines in diethyl ether

TABLE I

PERCENTAGE YIELDS OF AMINES FROM CHLOROAMINES AND ZINC ALKYLS IN DIETHYL ETHER SOLUTION

		Yields, %		
Chloroamines	Zinc alkyls	Primary amines	Secondary amines	Tertiary amines
CH_3NCl_2	$Zn(C_2H_5)_2$	78	17	...
$C_2H_5NCl_2$	$Zn(C_2H_5)_2$	71	17	...
n-$C_4H_9NCl_2$	$Zn(C_2H_5)_2$	76	18	...
i-$C_5H_{11}NCl_2$	$Zn(C_2H_5)_2$	78	16	...
n-$C_4H_9NCl_2$	$Zn(n\text{-}C_3H_7)_2$	61	24	...
$(n\text{-}C_4H_9)_2NCl$	$Zn(C_2H_5)_2$	..	71	1.5

TABLE II

PERCENTAGE YIELDS OF AMINES FROM CHLOROAMINES AND ZINC ALKYLS IN PETROLEUM ETHER SOLUTION

		Yields, %		
Chloroamines	Zinc alkyls	Primary amines	Secondary amines	Tertiary amines
CH_3NCl_2	$Zn(C_2H_5)_2$	44	46	...
$C_2H_5NCl_2$	$Zn(C_2H_5)_2$	49	42	...
n-$C_4H_9NCl_2$	$Zn(C_2H_5)_2$	57	43	...
i-$C_5H_{11}NCl_2$	$Zn(C_2H_5)_2$	52	42	...
$(C_2H_5)_2NCl$	$Zn(C_2H_5)_2$	..	70	1.8

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[1] Coleman and Hauser, THIS JOURNAL, **50**, 1193 (1928); Coleman and Yager, *ibid.*, **51**, 567 (1929).

[2] Coleman, *ibid.*, **55**, 3001 (1933).

[3] Tcherniak, *Bull. soc. chim.*, [2] **25**, 166 (1876).

and in petroleum ether solution are given in Tables I and II.

The percentage yields are calculated on the basis of the chloroamines. The zinc alkyls were always used in excess.

Experimental

Preparation of Chloroamines.—The method was essentially the same as that previously used in the work with Grignard reagents.[2] For the reactions in petroleum ether an ether boiling at 70–80° was used.

Preparation of Zinc Alkyls.—Diethyl zinc and di-*n*-propyl zinc were prepared by the method described by Noller.[4]

Reaction of Chloroamines with Zinc Alkyls.—The reaction of chloroamines with zinc alkyls was carried out by adding a cold solution of the chloroamine slowly and with stirring to an excess of a cold solution of the zinc alkyl in petroleum ether or diethyl ether. During the addition a flocculent white precipitate appeared. After completion of the reaction a slight excess of dilute sulfuric acid was slowly added. The aqueous layer was separated, made alkaline with sodium hydroxide and the mixture steam distilled. The distillate was collected in dilute hydrochloric acid and evaporated to dryness. After drying in a desiccator, the mixture of amine hydrochlorides was weighed and a portion used for determining the amounts of primary, secondary and tertiary amines present.

Separation of Amines in Reaction Products.—The mixtures of amine hydrochlorides were separated by the modification of Hinsberg's method previously used.[2]

Summary

1. Alkyl dichloroamines react with diethyl zinc to form primary and secondary amines.
2. Dialkyl chloroamines form secondary amines and very small yields of tertiary amines.
3. Petroleum ether is a better solvent for the reaction than diethyl ether.

IOWA CITY, IOWA RECEIVED MARCH 12, 1934

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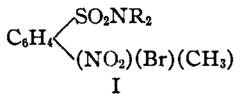
[4] Noller, "Organic Syntheses," 1932, Vol. XII, p. 86.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

A Comparison of the Activating Effect of the Sulfone Group with that of the Nitro Group

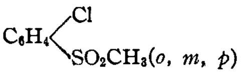
BY H. R. TODD AND R. L. SHRINER

A study of the alkaline hydrolysis of substituted benzene sulfonanilides (I) with nitro, bromo and methyl groups ortho and para to the sulfonamide grouping indicated that size and weight of the ortho groups were not factors in causing activation of the carbon–sulfur linkage as measured by ease of cleavage.[1] By far the most effective of these three was the nitro group and it was noted that this group differs from the other two in its very high dipole moment[2] ($\mu = 3.9 \times 10^{18}$). This suggested that the activating power might be correlated with the dipole moment. To test this theory a comparison of the influence of the sulfone group which has a still greater dipole moment[3] ($\mu = 5.05 \times 10^{18}$) was made with that of the nitro group. The influence of these two groups on the reactivity of a chlorine atom ortho, meta and para to each was studied: Formulas (II) and (III).



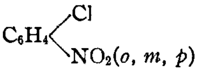
$C_6H_4\left<\begin{matrix}SO_2NR_2\\(NO_2)(Br)(CH_3)\end{matrix}\right.$

I



$C_6H_4\left<\begin{matrix}Cl\\SO_2CH_3(o,\ m,\ p)\end{matrix}\right.$

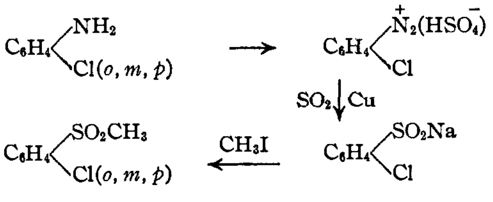
II



$C_6H_4\left<\begin{matrix}Cl\\NO_2(o,\ m,\ p)\end{matrix}\right.$

III

The three chlorophenyl methyl sulfones, which have not been previously described, were prepared by the following reactions



$$C_6H_4\left<\begin{matrix}NH_2\\Cl(o,m,p)\end{matrix}\right. \longrightarrow C_6H_4\left<\begin{matrix}\overset{+}{N}_2(H\overset{-}{SO_4})\\Cl\end{matrix}\right. \xrightarrow{SO_2,\ Cu} C_6H_4\left<\begin{matrix}SO_2Na\\Cl\end{matrix}\right. \xrightarrow{CH_3I} C_6H_4\left<\begin{matrix}SO_2CH_3\\Cl(o,m,p)\end{matrix}\right.$$

This general method of preparation for all three isomers was used in order to determine the utility of the reaction involving the replacement of the

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[1] Pezold, Schreiber and Shriner, THIS JOURNAL, **56**, 696 (1934).

[2] Williams, *Physik. Z.*, **29**, 174 (1928).

[3] DeVries and Rodebush, THIS JOURNAL, **53**, 2888 (1931).