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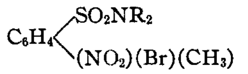
[4] Noller, "Organic Syntheses," 1932, Vol. XII, p. 86.

[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

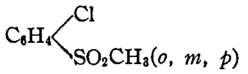
By H. R. Todd and R. L. Shriner

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).



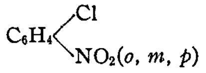
$C_6H_4\left\langle\begin{matrix} SO_2NR_2 \\ (NO_2)(Br)(CH_3) \end{matrix}\right.$

I



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

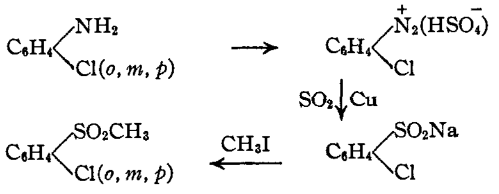
II



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

III

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



$$C_6H_4\left\langle\begin{matrix} NH_2 \\ Cl(o,m,p) \end{matrix}\right. \longrightarrow C_6H_4\left\langle\begin{matrix} \overset{+}{N_2}(H\overset{-}{SO_4}) \\ Cl \end{matrix}\right. \xrightarrow{SO_2,\ Cu} C_6H_4\left\langle\begin{matrix} SO_2Na \\ Cl \end{matrix}\right. \xrightarrow{CH_3I} C_6H_4\left\langle\begin{matrix} SO_2CH_3 \\ Cl(o,m,p) \end{matrix}\right.$$

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).

diazonium radical by the sulfinic acid group. Only the *o*-chlorophenyl methyl sulfinic acid was obtained in good yields (86%), the meta and para isomers being produced in 21 and 38% yields, respectively.

The reactivity of the halogen in each isomer was determined by measuring the rate of removal of the chlorine by alcoholic sodium ethoxide according to the procedure used by Franzen and Bockhacker[4] for determining the reactivities of chlorine in the nitrochlorobenzenes. The data obtained are summarized in Table I.

TABLE I

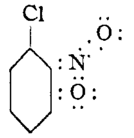
PERCENTAGE CHLORINE REMOVED BY ALCOHOLIC SODIUM ETHOXIDE

Compound	Time, hours 1	2	4	6
$ClC_6H_4NO_2$ ortho	24.70	33.43	36.47	36.72
$ClC_6H_4NO_2$ meta	0.49	0.75		
$ClC_6H_4NO_2$ para	26.21	34.90	41.69	42.86
$ClC_6H_4SO_2CH_3$ ortho	1.76	2.54	5.33	6.00
$ClC_6H_4SO_2CH_3$ meta	0.06	0.07		
$ClC_6H_4SO_2CH_3$ para	1.34	1.53	3.81	4.59

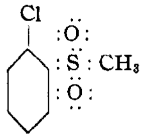
Consideration of the above data shows: (1) the nitro group has a very much greater activating effect on the halogen than the sulfone group; (2) in the case of the nitrochlorobenzenes the order of decreasing activity is $p > o > m$. In the case of the chlorophenyl methyl sulfones the order is $o > p > m$.

Since the dipole moment of the sulfone group is greater than that of the nitro group but the activating effect of the former is less than that of the latter it is evident that this physical property cannot be used as an index of activating effect.

The methyl sulfone group has recently been shown to be a meta directing group[5] contrary to the statement of Bourgeois and Abraham.[6] Hence the failure of this group to cause any pronounced activation must be connected with some peculiarities of its structure. According to Turner[7] the reason for the very pronounced activation caused by the nitro group is due to the presence of an oxygen atom bound by a true double bond (Formula IV) which may undergo addition reactions and it is to such addition compounds that Turner ascribes the remarkable influence of the nitro group. On the other hand, the sulfone group (V) has only semipolar linkages to the oxygen atoms which do not undergo addition reactions and, hence, should not cause activation.



IV



V

Experimental

Sodium *o*-, *m*- and *p*-Chlorophenyl Sulfinates.—A solution of 25 g. of the chloroaniline in 600 g. of 30% sulfuric acid was diazotized at 0° by the slow addition of a slight excess of 20% sodium nitrite solution. As the diazotization proceeded the solid amine sulfate gradually dissolved and a clear yellow solution resulted to which was slowly added an ice cold solution of 100 g. of concentrated sulfuric acid and 80 g. of water. Sulfur dioxide gas was passed into the solution until there was an increase in weight of 15 g. for each 100 cc. of solution. Then without interrupting the flow of sulfur dioxide and keeping the solution at 0–5°, copper bronze was added in small amounts until no more nitrogen was liberated. This was determined by interrupting the flow of sulfur dioxide momentarily and noting whether the copper sank to the bottom of the flask. The cold mixture was filtered and the precipitate vigorously stirred into 400 cc. of 10% sodium carbonate solution. Filtration and acidification of the filtrate gave the sulfinic acid which was dissolved in the calculated quantity of sodium hydroxide solution and evaporated. The yields were: sodium *o*-chlorophenylsulfinate, 38 g. or 86%; sodium *m*-chlorophenylsulfinate, 8 g. or 21%; sodium *p*-chlorophenylsulfinate, 15 g. or 38%.

***o*-, *m*- and *p*-Chlorophenyl Methyl Sulfones.**—The three sulfones were prepared by refluxing each of the above salts with an absolute alcohol solution of methyl iodide for four hours. Distillation of the alcohol and crystallization of the residue from water yielded the sulfones.

Compound	M. p., °C.	Sulfur analyses, % Calcd.	Found
o-$ClC_6H_4SO_2CH_3$	90	16.82	16.62
m-$ClC_6H_4SO_2CH_3$	106	16.82	16.74
p-$ClC_6H_4SO_2CH_3$	96	16.82	16.93

Determination of the Reactivity of the Halogens.—A 0.4 *N* solution of sodium ethoxide in absolute alcohol was prepared. In each of four Erlenmeyer flasks fitted with reflux condensers was placed 25 cc. of the sodium ethoxide solution. The solutions were heated by a hot plate and as soon as boiling started, a sample corresponding to 0.005 mole of the chlorophenyl methyl sulfone was added. At the end of one, two, four and six hours a flask was removed from the hot plate and the contents poured into 50 cc. of ice cold distilled water. This solution was acidified with nitric acid and filtered. The chloride in the filtrate was precipitated with silver nitrate and the silver chloride filtered, dried and weighed. The results were calculated as percentages of chlorine split off. Exactly the same procedure was followed for each of the chlorophenyl methyl sulfones and for *o*-, *m*- and *p*-nitrochlorobenzene. The results have already been given in Table I.

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[4] Franzen and Bockhacker, *Ber.*, **53**, 1175 (1920).

[5] Twist and Smiles, *J. Chem. Soc.*, **127**, 1248 (1925); Baldwin and Robinson, *ibid.*, **1445** (1932).

[6] Bourgeois and Abraham, *Rec. trav. chim.*, **30**, 407 (1911).

[7] Brewin and Turner, *J. Chem. Soc.*, 334 (1928).

Summary

1. The reactivity of the chlorine atom in *o*-, *m*- and *p*-chlorophenyl methyl sulfones toward sodium ethoxide has been determined and compared with the reactivity of the chlorine atom in *o*-, *m*- and *p*-nitrochlorobenzenes.

2. It was found that the activation of the halogen by the sulfone group was very much less than that produced by the nitro group.

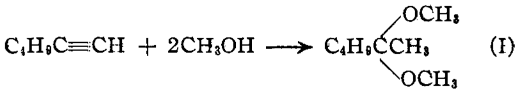
URBANA, ILLINOIS RECEIVED MARCH 12, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

The Preparation of Some Ketals of Alkylacetylenes with Methanol

BY D. B. KILLIAN, G. F. HENNION AND J. A. NIEUWLAND

The authors have recently shown[1] that *n*-butylacetylene reacts with methanol to form 2,2-dimethoxyhexane (I) in the presence of mercuric oxide and boron trifluoride.



$$C_4H_9C{\equiv}CH + 2CH_3OH \longrightarrow C_4H_9C(CH_3)(OCH_3)_2 \qquad (I)$$

This condensation is similar to the formation of acetals from acetylenes.[2]

This reaction has been studied in greater detail, and ketals have been prepared from methylacetylene, ethylacetylene, *n*-propylacetylene, *n*-butylacetylene and *n*-amylacetylene in high yield. All of the ketals are colorless liquids having highly characteristic odors. Both 2,2-dimethoxypropane and 2,2-dimethoxybutane possess odors similar to that of menthol.

The 2,2-dimethoxyalkanes are extremely unstable in the presence of acid and upon hydrolysis form methanol and the corresponding ketone $RCOCH_3$, where R represents the alkyl group attached to the ethynyl group in the acetylene. Since the catalyst is acidic, attempted neutralization of the reaction product with aqueous carbonate resulted in high yields of ketone. When anhydrous potassium carbonate was added to the reaction mixture before distillation, the ketal could be isolated without difficulty.[1]

Addition of monohydric alcohols other than methanol to alkylacetylenes in the presence of boron fluoride and mercuric oxide occurred rapidly, but the products were to a large extent polymeric. No ketals have thus far been isolated from such reactions. Ethyl alcohol, for example, reacted vigorously with amylacetylene, producing polymeric liquids of wide boiling range in addition to non-distillable resins.

With the exception of the first two, all of the compounds in Table I are new. For the sake of the completeness of the homologous series, dimethyl acetal[2] has been included in this table. Using acetone, methanol and formimido ether, Claisen[3] has previously prepared 2,2-dimethoxypropane.

TABLE I

PROPERTIES OF 2,2-DIMETHOXYALKANES, $R(CH_3)C(OCH_3)_2$

R	B. p., °C.	Mm.	Density	n_D	MR Calcd.	MR Found
H-	64–65		0.8494^{26}	1.3762^{26}	23.96	24.20
CH_3-	78–80	747	$.8448^{20}$	1.3746^{20}	28.58	28.18
C_2H_5-	48–50	100	$.8535^{28}$	1.3899^{28}	33.20	32.70
n-C_3H_7-	30–31	15	$.8494^{23}$	1.3986^{23}	37.81	37.71
n-C_4H_9-	58–60	30	$.8536^{25}$	1.4053^{25}	42.44	41.96
n-C_5H_{22}-	74–75	27	$.8543^{22}$	1.4122^{22}	47.05	46.67

TABLE II

ANALYSIS OF 2,2-DIMETHOXYALKANES

R	Empirical formula	Calcd., % C	Calcd., % H	Found, % C	Found, % H
C_2H_5-	$C_6H_{14}O_2$	60.96	11.95	60.75	11.68
n-C_3H_7-	$C_7H_{16}O_2$	63.57	12.21	63.21	12.14
n-C_4H_9-	$C_8H_{18}O_2$	65.69	12.41	65.56	12.18
n-C_5H_{11}-	$C_9H_{20}O_2$	67.40	12.87	67.94	12.47

The procedure for preparing the 2,2-dimethoxyalkanes is nearly uniform except that the temperature at which the reaction was carried out varied slightly according to the acetylene used. Two typical procedures are described.

Experimental Part

Reagents.—The preparation of the boron fluoride catalyst (in the form of $(C_2H_5)_2O{\cdot}BF_3$), alkylacetylenes, and the purification of the methanol, etc., have been described.[1,4] Methylacetylene and ethylacetylene were prepared by the action of the appropriate dialkyl sulfates on sodium acetylide in liquid ammonia and were purified by passing through water, dilute sulfuric acid, a calcium chloride tower and finally through soda lime. They

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(1) Hennion, Killian, *et al.*, THIS JOURNAL, **56**, 1130 (1934).

(2) Hinton and Nieuwland, *ibid.*, **52**, 2892 (1930).

(3) Claisen, *Ber.*, **31**, 1012 (1898).

(4) Hennion, Hinton and Nieuwland, THIS JOURNAL, **55**, 2858 (1933).