Alkali converts the tetraketone into a mixture which upon acidification yields carbon dioxide, mesitylglycolic acid, mesitylglyoxylic acid and a neutral compound which has not been identified.

URBANA, ILLINOIS RECEIVED FEBRUARY 28, 1934

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

The Nitration of α-Chloro and α-Bromoacetophenone

BY CHARLES BARKENBUS AND JOHN PHILIP CLEMENTS

m-Nitro-α-chloroacetophenone has been prepared with low yields by the action of diazomethane on *m*-nitrobenzoyl chloride[1] and by the chlorination of *m*-nitroacetophenone[2] though no yields were given. Since this compound was needed in fairly large amounts we have found that it can be prepared easily in good yields by the direct nitration of α-chloroacetophenone.

The nitration reaction has been widely used in studying orientation in the benzene ring. The most recent and interesting rule proposed for determining orientation in the benzene series is that of Latimer and Porter.[3] Since this rule neglects the influence of atoms beyond the so-called key atom the effect on nitration of the substitution of chlorine or bromine in the alpha position of acetophenone has been investigated. The results, listed in Table I, show that the introduction of chlorine or bromine does have some effect. This effect is not as large as that found in the nitration of esters of phenylacetic acid.[4]

TABLE I

PERCENTAGE OF META AND ORTHO-PARA ISOMERS FORMED DURING NITRATION

	Meta, %	Ortho-para, %
Acetophenone	65.5	34.5
α-Chloroacetophenone	68.5	31.5
α-Bromoacetophenone	69.4	30.6

These results are the average of several determinations.

Experimental

The method of determining the percentage of the different isomers formed during nitration has been worked out by Flurscheim and Holmes.[5] A modification of this method[4] was used though no consistent correction factor could be obtained and the extraction method had to be resorted to at that point. The data for a typical run on each of the three compounds are listed in Table II. The results stated in Table I are the average of at least three duplicate runs.

TABLE II

THE NITRATION, OXIDATION AND DETERMINATION OF THE ISOMERS

Substance	Acetophenone	α-Chloroacetophenone	α-Bromoacetophenone
Nitrated, g.	5.8576	7.3381	6.9592
Nitrated product obtained, g.	7.8530	9.3380	8.4880
Yield, %	97.6	98.5	99.4
Nitrated product oxidized, g.	2.8497	3.0000	3.5000
Acids obtained, g.	2.4802	2.0817	2.0680
Yield, %	86.0	83.0	86.5
Oxidation mixture, g.	0.4144	0.3610	0.3406
Nitrated product found by titration, g.	.4048	.3388	.3200
Unnitrated material present, g.	.0096	.0222	.0206
Unnitrated material (benzoic acid), %	2.32	6.15	6.05
2,4,6-Tribromoaniline obtained, g.	0.2760	0.2090	0.1941
Ortho and para nitrobenzoic acids, %	34.6	31.2	30.7
m-Nitrobenzoic acids, %	65.4	68.8	69.3

Preparation of *m*-Nitro-α-chloroacetophenone.—To 100 cc. of 96% sulfuric acid in a 500-cc. three-necked flask equipped with a dropping funnel and stirrer were added several pieces of carbon dioxide ice. The temperature dropped to at least −20° without outside cooling and could be easily kept at that temperature by further additions of the cooling agent. To this cold acid, 25 g. of α-chloroacetophenone of m. p. 57–58° was added slowly. When all of the solid had dissolved, a mixture of 20 cc. of 96% sulfuric acid and 15 cc. of fuming nitric acid (sp. gr. 1.50), cooled with carbon dioxide ice, was added rather rapidly, the temperature being kept below −20°. This required about twelve minutes and a longer period of addition was found to be detrimental. The solution was stirred for ten minutes at this temperature and then poured rapidly onto 500 g. of ice to which had been added some carbon dioxide ice. About 1200 cc. of ice water was then added and the light yellow solid filtered with suction and washed free from acid. The crude dry solid weighed 33 g. and was contaminated with unchanged α-chloroacetophenone, ortho and para isomers, and some benzoic acid.

[1] Dale and Nierenstein, *Ber.*, **60**, 1026 (1927).

[2] Baker, *J. Chem. Soc.*, **134**, 2416 (1931).

[3] Latimer and Porter, THIS JOURNAL, **52**, 206 (1930).

[4] Yabroff and Porter, *ibid.*, **54**, 1199, 2507 (1932).

[5] Flurscheim and Holmes, *J. Chem. Soc.*, **131**, 448 (1928).

The crude product was purified by refluxing with 50 cc. of ether for one hour, then cooled in an ice-bath and filtered. The solid was washed with a little ice-cold ether and dried; m. p. 100.5–102°; 25 g., 77%.

Summary

The orientating effect of chlorine and bromine in the alpha position of acetophenone has been investigated and found to be slight in the case of nitration. *m*-Nitro-α-chloroacetophenone has been prepared in good yields by the direct nitration of α-chloroacetophenone.

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO, AND THE FERTILIZER AND FIXED NITROGEN INVESTIGATIONS DIVISION, BUREAU OF CHEMISTRY AND SOILS]

Factors Governing the Instability of a Carbon to Nitrogen Bond. I. The Instability of the Carbon to Nitrogen Bond in Substituted Methyl Amines[1]

BY M. S. KHARASCH AND LOUIS B. HOWARD

Introduction

In previous communications[2] has been discussed our hypothesis of the nature of the carbon-to-carbon bond in organic compounds. The extension of our concept to the problem of the stability or instability of the carbon-to-nitrogen bond in compounds of the type R-NH_2 is possible without further subsidiary hypotheses. The treatment of the subject matter is particularly simplified if one bears in mind that the bonding electrons of both carbon and nitrogen are in the L-shell, and that the NH_2 group acts as a strongly electronegative radical.[3]

Furthermore, from data available in the literature an exceedingly important deduction may be made, namely, the effects of attached radicals on the electronegativity of the nitrogen atom follow the same rules which have been evolved for the carbon atom; *i. e.*, strongly electronegative radicals attached to either carbon or nitrogen atoms decrease their electronegativity. It is quite evident, therefore, that in a group R_2N- if the radical R is strongly electronegative the group as a whole becomes weakly electronegative. The validity of this generalization is supported by the dissociation in inert solvents of some triarylmethyldiarylamines $(C_6H_5)_3C{=}N(C_6H_5)_2$ and tetraarylhydrazines studied by Wieland.[4] Thus, with the exception of tetrakis-(*p*-biphenyl)-hydrazine, the tendency toward dissociation of eight tetraarylhydrazines studied by Wieland and co-workers,[5] follows the order predictable upon the basis of the relative electronegativities of the radicals attached to the nitrogen atoms. The volumes or weights of the substituent groups appear to have as little significance as in the case of hexaarylethane dissociation.

Method of Study.—As a means of estimating the effects of different radicals on the stability of the carbon-to-amino bond, a study of the rate of hydrolysis of the amines in dilute acid at relatively low temperatures was made. We were cognizant of the difficulties involved in the interpretation of such results. The method, however, was considered adequate since we were trying to bring into relief factors of first magnitude.

Our study included the rate of hydrolysis of the following amines, using 0.05 *N* hydrochloric acid: (1) $(CH_3)_3CNH_2$, (2) $(CH_3)_2CH(C_6H_5)NH_2$, (3) $CH_3(C_6H_5)_2CHNH_2$, (4) $(C_6H_5)_3CNH_2$, (5) $(C_6H_5)CNHC_2H_5$.

Of these amines, 1, 2 and 3 were unaffected by 50 or 100 hours of heating at 100°. Triphenylmethylamine, on the other hand, was found to be hydrolyzed to the following extent:

Time in minutes	15	30	45	60	75	90
Hydrolyzed, %	22	40	58	70	80	85

With these facts as a background, the study of amines containing methyl substituents more electronegative than the phenyl radical appeared to be in order. The β-naphtholphenylmethylamine group readily suggested itself, for some of our other work had indicated that the β-naphthol group is very strongly electronegative.

In the case of those compounds it was thought

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(1) Abstracted from a dissertation submitted by Louis B. Howard to the Faculty of the Graduate School of the University of Chicago in March, 1931, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) For pertinent references consult the paper by Kharasch, Reinmuth and Mayo, *J. Chem. Ed.*, **11**, 82 (1934).

(3) Salt formation in general decreases tremendously the electronegative character of the amino group, and correspondingly the concomitant effect of that group on the other bonds in the molecule.

(4) Wieland, *Ann.*, **381**, 214 (1911).

(5) Wieland, "Die Hydrazine," Verlag von Ferdinand Enke, Stuttgart, 1913.