The course of the condensation has been shown to be a series of condensations and subsequent rearrangements.

NOTRE DAME, INDIANA RECEIVED MAY 7, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Reactive Methyl Group in Toluene Derivatives. I. Oxidation with Selenium Dioxide and Cleavage of Benzylpyridinium Halides

BY C. HAROLD FISHER

That certain toluenes possess an active methyl group,[1] comparable in some cases with the methyl group of acetophenone, has been long known. The results of a further study of the reactivity of the toluene methyl group are reported below under separate headings.

Oxidation with Selenium Dioxide.—It was found that conditions more drastic than those required for acetophenone[2] (refluxing in alcohol solution) are necessary for oxidation of toluene derivatives. Even 2,4-dinitrotoluene and 2,4,6-trinitrotoluene, which might be expected to give either nitrobenzaldehydes or nitrocresols,[3] were unattacked by selenium dioxide in boiling alcohol, and in boiling dioxane. However, it was found possible in several cases to cause oxidation at higher temperatures. At the refluxing temperature *p*-nitrotoluene was converted in poor yield into *p*-nitrobenzoic acid. Oxidation proceeded more satisfactorily and under less drastic conditions in the case of the benzyl halides. Nitrobenzaldehyde was obtained in good yield from *p*-nitrobenzyl bromide, and benzyl chloride was oxidized to benzaldehyde and a small amount of benzoic acid. Whether these benzyl halides were oxidized as such or underwent a preliminary hydrolysis to the corresponding benzyl alcohol[4] is not known. The oxidation of *p*-nitrobenzal bromide was more difficult than that of *p*-nitrobenzyl bromide; the product was *p*-nitrobenzoic acid. To ascertain the effect of additional phenyl and nitrophenyl groups the oxidation of diphenylmethane, 4,4′-dinitrodiphenylmethane and triphenylmethane was studied. It was found that none of these substances is oxidized by selenium dioxide in boiling alcohol, but that diphenylmethane and triphenylmethane are converted into benzophenone and triphenylcarbinol, respectively, at higher temperatures.

Cleavage of Benzylpyridinium Halides.—The halomethyl group of phenacyl halides[5] is quickly replaced by an hydroxyl group by condensation with pyridine and treatment with alkali of the pyridinium salt thus formed. The corresponding transformation (*p*-nitrobenzyl halide into *p*-nitrophenol) was not caused by the action of either alkali or alkaline hypobromite on the *p*-nitrobenzylpyridinium halides. No alkali-soluble products were formed with alkali treatment. However, alkaline hypobromite reacted almost at once with *p*-nitrobenzylpyridinium bromide, and with the corresponding chloride, to give good yields of *p*-nitrobenzoic acid. That this conversion of *p*-nitrobenzylpyridinium halides into *p*-nitrobenzoic acid proceeds through a brominated intermediate instead of by direct oxidation is suggested by the speed of the reaction, and the behavior of *p*-nitrobenzylpyridinium bromide toward bromine water: at once there was formed a yellow, flocculent precipitate which in turn reacted with alkaline hypobromite to give a good yield of *p*-nitrobenzoic acid. Apparently the nitro group is necessary for this transformation, since benzyl pyridinium chloride under the same conditions was found to yield resinous products, of which only a negligible portion was alkali-soluble.

Experimental

Selenium Dioxide Oxidations.—In the experiments described below equimolar quantities of the toluene derivative (0.05–0.1 mole) and selenium dioxide were dissolved in alcohol under an air-cooled return condenser, and the temperature of the mixture was brought to the desired value with an oil-bath or free flame, allowing some or all the alcohol to distil. Some products (benzoic acid and *p*-nitrobenzaldehyde) were isolated by extraction with hot water. Triphenylcarbinol was separated from selenium by filtering a hot alcohol solution; the liquid products were decanted and distilled. The phenylhydrazones of benzaldehyde and *p*-nitrobenzaldehyde melted, respectively, at 154–155.5° and 158.5–159.5°. Benzoic acid in

---

[1] For references see Chardonnens, *Helv. Chim. Acta*, **16**, 1295 (1933).

[2] Riley, Morley and Friend, *J. Chem. Soc.*, 1875 (1932).

[3] Hepp, *Ann.*, **215**, 344 (1882).

[4] Astin, Newman and Riley, *J. Chem. Soc.*, 391 (1933).

[5] Babcock and Fuson, THIS JOURNAL, **55**, 2946 (1933); Kröhnke, *Ber.*, **66**, 1386 (1933).

3% yield was obtained along with benzaldehyde from benzyl chloride. All solids were identified by the mixed melting point method. A vigorous reaction, causing distillation, set in soon after distillation of the solvent from diphenylmethane and selenium dioxide; the reaction mixture remaining in the flask was nearly pure benzophenone. Other data are given in the table.

Toluene derivative	Reaction temp., °C.	Time, hours	Product	M. p., °C.	Yield, %
p-Nitrobenzyl bromide	140–150°	2	*p*-Nitrobenzaldehyde	105–106	56
Benzyl chloride	Refluxed without solvent	3	Benzaldehyde	(B. p. 173–180)	49
Diphenylmethane			Benzophenone	47–48.5 (b. p. 294–298°)	47
Triphenylmethane	Refluxed without solvent	0.2	Triphenylcarbinol	160–162	15

Reaction of Hypobromite with Benzylpyridinium Halides.—Two grams of *p*-nitrobenzylpyridinium chloride in 20 cc. of water was treated with hypobromite (100 cc. of water, 10 g. of sodium hydroxide and 3 cc. of bromine). At once the reaction mixture was washed with ether, and the aqueous layer acidified. Bromine was removed with sodium bisulfite, and dissolved ether by boiling. The precipitate thus obtained melted at 237–238.5° (mixed m. p. with *p*-nitrobenzoic acid was not depressed), and amounted to 1.1 g. (82%).

The other hypobromite reactions were carried out in a similar fashion.

Summary

The action of selenium dioxide on several toluenes and of alkali and hypobromite on certain benzylpyridinium halides has been studied. It was found that oxidation with selenium dioxide proceeds with greater difficulty than in the case of acetophenone; and that alkaline hypobromite converts *p*-nitrobenzylpyridinium halides into *p*-nitrobenzoic acid in good yield.

CAMBRIDGE, MASS. RECEIVED MAY 8, 1934

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

The Chemistry of Organic Gold Compounds. V. Auration of Aromatic Nitriles

BY M. S. KHARASCH AND THOMAS M. BECK[1,2]

Introduction

Kharasch and Isbell, in their investigation of organic gold compounds,[3] discovered that certain derivatives of auric chloride of the type $RAuCl_2$ (R being an aromatic radical), which cannot be prepared by the usual Grignard reaction, may be prepared by the direct action of anhydrous auric chloride on the organic compound. For example, phenyl auric dichloride is readily obtained by the action of auric chloride on benzene. It was further pointed out that a definite relation exists between the stability of the various substituted phenyl auric dichlorides and the relative electronegativities of the R groups,[4] in that the more highly electronegative radicals give compounds too unstable to be isolated, and that the hydrides of the least electronegative radicals are too unreactive with auric chloride. In general, the preparation by this method of compounds of the type described was limited to benzene derivatives whose substituent radical lies between tolyl and nitrophenyl in electronegativity.

In an extension of this work, an investigation of the action of auric chloride on weakly electronegative radicals of the benzene series was undertaken. This paper deals with the direct auration of aromatic nitriles, the position taken by the gold, and the stability of the gold–carbon bond toward a variety of chemical reagents.

Previous Work on the Action of Auric Chloride on Nitriles.—Henke[5] investigated the reaction of auric chloride with aceto-, propio- and benzonitriles, reporting the formation of molecular complexes of the type $RCN \cdot AuCl_3$. However, he does not specify whether his auric chloride was anhydrous; furthermore, his analytical results do not justify the assigned formulas.

Lenher[6] states that methyl, ethyl, benzyl and phenyl cyanides each extract auric chloride from its aqueous solutions without reducing the gold. Obviously his gold chloride was hydrated, and consequently his observations have no bearing upon the work described in this investigation.

---

(1) This communication is an abstract of a dissertation submitted by Thomas M. Beck in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Chicago, 1932.

(2) The authors wish to take this opportunity to express their appreciation to the Eli Lilly Company of Indianapolis for support which made this work possible.

(3) Kharasch and Isbell, THIS JOURNAL, **53**, 3053 (1931).

(4) Kharasch and Reinmuth, *J. Chem. Educ.*, **8**, 1713 (1931), Kharasch, Reinmuth and Mayo, *ibid.*, **11**, 88 (1934).

(5) Henke, *Ann.*, **106**, 280 (1858).

(6) Lenher, THIS JOURNAL, **35**, 549 (1913).