

ÉTARD REACTION

I. ITS SCOPE AND LIMITATION WITH SUBSTITUTED TOLUENES¹

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ABSTRACT

The scope and limitations of the Étard oxidation of substituted toluenes to substituted benzaldehydes by chromyl chloride have been studied. The conditions of the reaction were investigated and an improved method of performing it was developed.

INTRODUCTION

Though the chromyl chloride oxidation of toluenes to benzaldehydes was discovered by Étard in 1877 (1, 2) the reaction has been little used and no systematic study has been made of its potentialities. In connection with other work it was necessary to prepare a series of substituted benzaldehydes and this method seemed the most general and convenient. Accordingly a study of its scope and limitations for the conversion of substituted toluenes to substituted benzaldehydes was carried out.

The procedure used is to add a solution of chromyl chloride to a stirred solution of the toluene. The solvents usually used are carbon tetrachloride (3, 4, 5), carbon disulphide (6, 7, 8, 9), and chloroform. Carbon disulphide has the disadvantage of a low boiling point. The chloroform must be free from preservative alcohol and also was found to give troublesome emulsions during working up. In preliminary experiments the yields were little different with each solvent and carbon tetrachloride was therefore chosen as the general solvent for the study.

A complex is formed as intermediate in the reaction and this must be hydrolyzed under reducing conditions to prevent oxidation of the benzaldehyde to a benzoic acid. Saturated aqueous sodium sulphite (3) was the most convenient, but the aqueous solution must be well cooled and stirred during addition to prevent overoxidation. It has been recommended (3) that the complex be isolated by filtration and decomposed separately. This gives a purer product, since the complex contains no unreacted toluene, but the decomposition was found to be less easily controlled than when carried out with the complex suspended in the original solvent.

During the exothermic addition of chromyl chloride to the toluene, the initial dark red color of the solution becomes dark brown to black as the complex is slowly precipitated. These observations suggest that the initial step is the formation of a π - or σ -complex between the aromatic and chromyl chloride, which is followed by the formation of the true solid complex. (Spectroscopic evidence has been obtained for the rapid formation of a soluble complex (10).) It has been the usual practice to allow the reaction mixture to stand for a period of a few days (3, 11) to several weeks (4, 8) to allow complete separation of the complex. However, if sufficient time is allowed for formation of the physical complex, it should be possible to accelerate the second step of formation of the solid complex without harm to the aromatic nucleus, by heating the reaction mixture. This has been found to be the case and the reaction time can be considerably reduced by allowing the mixture to stand a short time and then refluxing it for several hours. Reaction times of 2 to 12 hours only are then required and this makes the reaction

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a very convenient one. If the reaction mixture is not initially cooled, or is heated too soon after the chromyl chloride is added, a vigorous or explosive reaction can occur.

To study the scope of the reaction with various toluenes the addition was carried out as usual and the mixture allowed to stand overnight. The product was isolated in the normal way and the aldehyde content estimated gravimetrically with 2,4-dinitrophenylhydrazine reagent. In the preparative experiments the mixture was refluxed for several hours before decomposition. The optimum conditions of reaction were generally not determined though enough data (Table I) were collected to predict them. In the case of *p*-iodotoluene the most suitable conditions are reported.

TABLE I

	Toluene	Temp. ^a	Time ^b	Yield ^c	Conversion ^d
I	<i>o</i> -Methyl	R.T.	<i>o.n.</i>	28	51
II	<i>m</i> -Methyl	R.T.	<i>o.n.</i>	32	50
III	<i>p</i> -Methyl	R.T.	<i>o.n.</i>	35	45
IV	<i>p</i> -Fluoro	R.T.	3 days	85	40
V	<i>o</i> -Chloro	R.T.	<i>o.n.</i>	79	19
VI	<i>o</i> -Chloro	Reflux	6 hr.	58	90
VII	<i>p</i> -Chloro	R.T.	2 hr.	100	0
VIII	<i>p</i> -Chloro	R.T.	3 days	86	36
IX	<i>p</i> -Chloro	Reflux	4 hr.	78	95
X	<i>o</i> -Bromo	Reflux	6 hr.	60	95
XI	<i>p</i> -Bromo	R.T.	<i>o.n.</i>	87	23
XII	<i>p</i> -Bromo	Reflux	6 hr.	85	92
XIII	<i>o</i> -Iodo	R.T.	3½ days	50	6
XIV	<i>o</i> -Iodo	Reflux	15 hr.	56	24
XV	<i>p</i> -Iodo	R.T.	<i>o.n.</i>	77	10
XVI	<i>p</i> -Iodo	R.T.	3 days	72	25
XVII	<i>p</i> -Iodo	R.T.	7 days	65	50
XVIII	<i>p</i> -Iodo	Reflux	4 hr.	90	42
XIX	<i>p</i> -Iodo	Reflux	10 hr.	83	85
XX	<i>o</i> -Nitro	Reflux	10 hr.	45	15
XXI	<i>p</i> -Nitro	Reflux	10 hr.	36	26
XXII	<i>p</i> -Methoxy	R.T.	<i>o.n.</i>	7	0
XXIII	<i>p</i> -Hydroxy	R.T.	<i>o.n.</i>	20	0
XXIV	<i>p</i> -Mercapto	R.T.	<i>o.n.</i>	50	0
XXV	<i>p</i> -Chloromethyl	R.T.	<i>o.n.</i>	32	10 ^e
XXVI	<i>p</i> -Cyano	R.T.	<i>o.n.</i>	35	<5
XXVII	<i>p</i> -Cyano	R.T.	3 days	22	5 ^f

^aR.T. denotes room temperature (22°–25°).

^b*o.n.* denotes stirring overnight.

^cPercentage yield of distillable product.

^dPercentage of aldehyde in product.

^eDerivative *m.p.* ca. 258°. *p*-Tolualdehyde 2,4-dinitrophenylhydrazone has *m.p.* 232.5°–234.5°, Ref. 22.

^fSolid *m.p.* 211°–214°. *p*-Cyanobenzoic acid has *m.p.* 219°, Ref. 23.

The three isomeric xylenes (I–III) all give tolualdehydes with oxidation of only one methyl group, as previously observed (3, 11), since the complex precipitates and further reaction is prevented. The yields and conversions are little different for all three. For the series *p*-fluoro-, *p*-chloro-, *p*-bromo-, and *p*-iodo-toluene (IV, VII, VIII, XI, XV, XVI, XVII) the yields decrease progressively for reaction at room temperature. Good conversions are obtained for *p*-chlorotoluene by refluxing for 4 hours (IX), whereas *p*-bromotoluene requires 6 hours (XII), and *p*-iodotoluene requires some 10 hours (XVIII, XIX). In these cases the yields of recovered product are all good (>80%) and the aromatic nucleus is not destroyed by prolonged refluxing. In the case of the ortho-halogenated toluenes the increasing size of the halogeno atom for the series chlorine, bromine, and iodine results in a considerably decreasing ease of oxidation (V, VI, X, XIII, XIV). Good

conversions can be obtained in the case of *o*-chloro- (V, VI) and *o*-bromo-toluene (X) by refluxing, but *o*-iodotoluene (XIII) is only oxidized very slowly, and prolonged reaction (XIV) tends to destroy the entire molecule.

p-Nitrotoluene is only slowly oxidized (XXI) and the ortho-isomer less so (XX). This must be due to the deactivating effect of a nitro group on an aromatic ring (12).

Of the other substituted toluenes investigated (XXII–XXVII), none of them gave any useful yield of a substituted benzaldehyde. Very little methoxytoluene (XXII) was recovered from its reaction with chromyl chloride. The major product was an undistillable polymer, and the chromyl chloride, which is a strong Lewis acid, must have caused polymerization. However, in the case of *p*-cresol (XXIII) and *p*-thiocresol (XXIV), though no aldehyde was formed, increased quantities of starting material could be recovered.

In the oxidation of *p*-chloromethyltoluene only some 30% of product could be obtained, but this analyzed for 10% of aldehyde. The 2,4-dinitrophenylhydrazone seemed to be that of *p*-chloromethylbenzaldehyde, since it had a higher melting point than that of *p*-tolualdehyde, the other possible product, suggesting that the methyl and not the chloromethyl group had been attacked.

p-Toluonitrile (XXVI, XXVII) was largely destroyed by reaction with chromyl chloride but a small amount of *p*-cyanobenzoic acid could be isolated.

In many cases the Étard reaction provides a simple and convenient one-step method of converting a toluene to a benzaldehyde. This gives better yields than the corresponding oxidations with manganese dioxide (3, 13) in sulphuric acid or electrolytically (3), and is simpler than the two-stage conversions of side-chain bromination and hydrolysis (14) and of oxidation with chromium trioxide in acetic anhydride followed by hydrolysis of the resulting diacetate (15).

EXPERIMENTAL

Chromyl Chloride

Chromyl chloride was a gift from the Mutual Chemical Division of the Allied Chemical Corporation, and was used as received.

Toluenes

Most of these were commercial samples, which were distilled before use. Some were made by a Sandmeyer reaction from the appropriate toluidines (16, 17).

p-Methoxytoluene

p-Cresol (21.6 g.) was dissolved in water (100 ml.) containing sodium hydroxide (8.3 g.). The mixture was cooled to 10° C. and methyl sulphate (27.0 g.) was added dropwise with stirring over 1/2 hour (18). The mixture was heated under reflux for 2 hours, cooled, diluted with water, and then extracted with ether. Isolation of the product gave 19.5 g. (80%), b.p. 163°–165° at 580 mm., n_D^{21} 1.5112 (lit. b.p. 175°–177° (19)).

p-Chloromethyltoluene

A mixture of toluene (70 g.), paraformaldehyde (6 g.), and pulverized zinc chloride (6 g.) was heated to 60°, and a stream of gaseous hydrogen chloride passed in (20) for 20 minutes. The product (25 g.) had b.p. 88°–90° at 18 mm.

Oxidations with Chromyl Chloride

In a typical experiment the toluene (1/10–1/5 mole) was dissolved in carbon tetrachloride (5–6 volumes). Chromyl chloride (0.21–0.42 mole) in an equal volume of carbon

tetrachloride was added slowly over 1 hour with stirring and external cooling in a bath of cold water so that the temperature never rose above 35°. Stirring was continued for another 2 hours and the mixture was then either allowed to stand at room temperature or refluxed with stirring for a number of hours. If the reaction is *not initially cooled* or if stirring is discontinued too soon, a *violent or explosive reaction* may take place. The reaction mixture was decomposed by pouring onto a stirred mixture of ice and saturated aqueous sodium sulphite solution. The use of insufficient ice or stirring may lead to overheating and overoxidation of the benzaldehyde to the benzoic acid. The organic layer was separated and the aqueous layer extracted several times with carbon tetrachloride. Extraction is sometimes made difficult by the precipitation of basic chromium salts, and these can best be removed by adding diluted (1:1) hydrochloric acid. The products were isolated by distillation and their content of benzaldehydes determined by treating a portion with 2,4-dinitrophenylhydrazine sulphate dissolved in aqueous methanol. The precipitates formed on warming were washed with water and cold methanol and dried at 100° before they were weighed.

p-Iodobenzaldehyde

A solution of *p*-iodotoluene (43.6 g., 0.2 mole) in carbon tetrachloride (150 ml.) was placed in a three-necked flask, immersed in ice-cold water. Chromyl chloride (65.2 g., 0.42 mole) in carbon tetrachloride (150 ml.) was allowed to run in dropwise, with good stirring, during 1 hour. The mixture was stirred at room temperature for a further 1 hour, and then heated slowly to reflux during another 1 hour. The mixture was stirred while refluxing for a further 20 hours. The cooled reaction mixture was poured slowly with vigorous stirring by hand onto sodium sulphite (60 g.) dissolved in water (300 ml.) containing ice (300 g.). Diluted (1:1) hydrochloric acid (100 ml.) was added to dissolve the basic chromium salts, and the organic layer separated and the aqueous layer extracted three times with portions of carbon tetrachloride. The combined organic solution was washed with water and dried. The residue left when the solvent was removed was distilled, giving the product, b.p. 145°–150° at 25 mm., m.p. 55°–65° (27.0–30.0 g., 58–64%). A forerun, b.p. 125°–130° at 25 mm. (3.5–5.0 g.) was largely unchanged *p*-iodotoluene. The *p*-iodobenzaldehyde can be recrystallized from aqueous ethanol to m.p. 75° (lit. m.p. 77°–78° (21)).

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