by extraction with diethyl ether followed by drying of the solution over $MgSO_4$.

In general, product identification was based on nmr analysis of the crude reaction mixtures and vpc retention times by comparison with known compounds. 1,1,2-Triphenylethanol, mp 88–89°, mmp 88–89° (lit.[15] mp 88–89°), was also identified as the major product from the reductions in the presence of air by column chromatography of the crude reaction mixture on silica gel using hexane as eluent, followed by recrystallization from hexane and comparison of its ir and nmr spectra with those of an authentic sample.

The following procedure was followed for reactions carried out on a high vacuum line. The mercurial **1** and the basic aqueous sodium borohydride solutions were mixed in a flask followed by six freeze–evacuate–thaw cycles to remove dissolved oxygen and other gases. A degassed flask of tetrahydrofuran over lithium aluminum hydride was then opened to the manifold and the desired amount of tetrahydrofuran was flash distilled into the reaction flask. The evacuated flask was then isolated from the vacuum system and stirred for the desired period. Normal work-up procedure followed.

It is noteworthy that, contrary to previous reports regarding reductions in aqueous solution,[16] significant gas evolution was observed in all sodium borohydride reductions carried out in aqueous tetrahydrofuran. This indicates that diborane may be produced since it would be rapidly hydrolyzed with evolution of hydrogen under the reaction conditions.[17]

Reduction of 1 with Lithium Aluminum Hydride and Sodium Bis(2-methoxyethoxy)aluminum Hydride.—The reductions of the organomercurial **1** with lithium aluminum hydride and sodium bis(2-methoxyethoxy)aluminum hydride were carried out in freshly distilled tetrahydrofuran under an argon atmosphere. After stirring for several hours the reaction mixtures were quenched with 10% H_2SO_4, extracted with diethyl ether, dried over $MgSO_4$, and analyzed by vpc and nmr.

Reduction of the Organomercurial with Sodium Amalgam.—The reduction of 2,2,2-triphenylethylmercuric chloride with 1.5% sodium amalgam was carried out according to the procedure of Sokolov, Rodina, and Reutov.[18] The products were recovered by extraction with diethyl ether followed by drying with $MgSO_4$.

Registry No.—**1**, 35341-90-3; sodium borohydride, 16940-66-2.

(15) C. Hell and F. Wiegandt, *Chem. Ber.*, **37**, 1429 (1904).

(16) F. G. Bordwell and M. L. Douglass, *J. Amer. Chem. Soc.*, **88**, 993 (1966).

(17) A. Stock and K. Friederici, *Chem. Ber.*, **46**, 1959 (1913).

(18) V. I. Sokolov, N. B. Rodina, and O. A. Reutov, *J. Organometal. Chem.*, **17**, 477 (1969).

Hydrogenolysis of Aromatic Halides with Thiophenol

MARVIN W. BARKER,* SUSAN C. LAUDERDALE,[1a] AND JOSEPH R. WEST[1b]

Department of Chemistry, Mississippi State University, State College, Mississippi 39762

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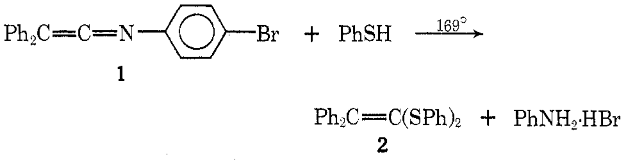
The hydrogenolysis of aromatic halides has received attention both as a mechanistic curiosity[2] and as a synthetic tool.[3] Reagents employed for halide hydrogenolyses include Friedel–Crafts catalysts,[2] triphenylphosphine,[4] triphenyltin hydride,[3] and standard reducing agents such as Raney nickel with base, hydrogen iodide, and catalytic systems. Of these reagents, only the triphenyltin hydride system offers much synthetic utility. We wish to report an additional system for effecting hydrogenolysis of aromatic halides.

In an investigation of the reaction of ketenimines with thiols, we observed that treatment of diphenylketene-*N*-(*p*-bromophenyl)imine (**1**) with excess thiophenol at 169° resulted in the production of diphenylketene diphenylmercaptal (**2**) and aniline hydrobromide in 84% yields, respectively.[5] To test the utility of the unexpected debromination observed, a series of model aromatic halides was treated with thiophenol.



The *o*- and *p*-bromoanilines and *p*-iodoaniline were found to undergo hydrogenolysis readily in refluxing thiophenol to produce aniline hydrobromine and aniline hydriodide in 78%, 88%, and quantitative yields, respectively. Only a 15.8% yield was obtained with *p*-chloroaniline, and no aniline hydrohalide was obtained from the treatment of *p*-fluoro- or *m*-bromoaniline with thiophenol. Hydrogenolysis of iodine also occurs with *p*-iodonitrobenzene (44.3%) and, in fact, with iodobenzene (9.0%). However, *p*-bromonitrobenzene did not undergo this reaction.

The results indicate that the ease of halogen removal is $I > Br > Cl > F$, and that haloanilines undergo hydrogenolysis of the halide more easily than halonitrobenzenes, which undergo hydrogenolysis of the halide more easily than halobenzenes. Although no mechanistic study has been undertaken on the reaction, the observation that radical initiators do not effect the reaction at a lower temperature leads one to lean toward an ionic mechanism such as has been demonstrated for the triphenylphosphine hydrogenolysis of aromatic halides.[4] The greater facility of hydrogenolysis of the iodide on *p*-iodonitrobenzene compared to iodobenzene would indicate the advantage of having an electron-withdrawing substituent in the para position and would suggest that the anilines may well be protonated prior to hydrogenolysis of the halide.

The excellent yields obtained for the hydrogenolysis of haloanilines with thiophenol and the reported utility of the triphenyltin hydride hydrogenolysis of other aromatic halides offer good synthetic procedures for the hydrogenolysis of bromo- and iodo-substituted compounds. In essence, thiophenol can be used effectively on aniline compounds for which the use of the tin hydride system is limited.

Experimental Section

Hydrogenolysis of Haloanilines.—The following procedure for the hydrogenolysis of *p*-bromoaniline with thiophenol typifies the method used for all haloanilines. A solution of 5.0 g (0.028 mol) of *p*-bromoaniline in 20 ml of freshly distilled thiophenol was heated to reflux for 3 hr. During reflux, aniline hydrobromide precipitated. The reaction mixture was cooled and the solid was collected to yield 4.4 g (88%) of aniline hydrobromide which was identical (ir and mixture melting point) with an authentic sample.

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(1) (a) NDEA Predoctoral Fellow. (b) Taken in part from the Ph.D. Dissertation of J. R. W., Mississippi State University, Aug 1970.

(2) G. R. Pettit and D. M. Piatak, *J. Org. Chem.*, **25**, 721 (1960).

(3) D. H. Lorenz, P. Shapiro, A. Stern, and E. I. Becker, *ibid.*, **28**, 2332 (1963); G. F. Karabatsos, R. L. Shone, and S. E. Scheppele, *Tetrahedron Lett.*, 2113 (1964).

(4) H. Hoffmann and D. Michael, *Ber.*, **95**, 528 (1962).

(5) M. W. Barker and J. R. West, Abstracts, 21st Southeastern Regional Meeting of the American Chemical Society, Richmond, Va., 1969, Paper 204.

Under similar conditions *p*-iodoaniline yielded a quantitative amount of aniline hydroiodide in 1 hr, *o*-bromoaniline produced a 78.4% yield of aniline hydrobromide in 6 hr, and *p*-chloroaniline produced a 15.8% yield of aniline hydrochloride in 96 hr. Neither *p*-fluoro- nor *m*-bromoaniline showed evidence of hydrogenolysis with thiophenol.

Hydrogenolysis of *p*-Iodonitrobenzene.—A mixture of 6.1 g (0.024 mol) of *p*-iodonitrobenzene, 10 ml of thiophenol, and 10 ml of aniline was heated to reflux for 17 hr. Aniline hydriodide (2.4 g, 44.3%) was isolated from the reaction mixture by aqueous extraction. Under similar conditions, *p*-bromonitrobenzene gave no evidence for hydrogenolysis.

A similar reaction without ainiline was studied to see if nitrobenzene could be isolated from the hydrogenolysis of *p*-iodonitrobenzene. A solution of 10 g (0.04 mol) of *p*-iodonitrobenzene and 60 ml of thiophenol was refluxed for 7 hr. The precipitate formed was collected, washed with ether, and dissolved in water. The solution was made alkaline with NaOH and extracted with ether. Removal of the solvent left 1 g (27% yield) of aniline identified by retention time on a 6-ft 3% SE-30 column at 100° in a Hewlett-Packard Model 402 gas chromatograph. Apparently an oxidation–reduction reaction occurs between thiophenol and the nitro group. No nitrobenzene was observed in the gc. Treatment of nitrobenzene with thiophenol under similar conditions gave little aniline; thus the reduction observed must be intimately associated with the hydrogenolysis reaction.

Hydrogenolysis of Iodobenzene.—A solution of 10.0 g (0.05 mol) of iodobenzene, 10 ml of thiophenol, and 10 ml of aniline was heated to reflux for 7 days. Aniline hydriodide (1.0 g, 9.0% yield) was isolated from the reaction mixture by collection of the solid. From a similar reaction, a gc of the filtrate on a 6-ft 3% SE-30 column at 65° in a Hewlett-Packard Model 402 gas chromatograph showed the presence of a small amount of benzene identified by retention time of an authentic sample.

Attempted Radical Initiation.—No reaction between thiophenol and *p*-bromoaniline was observed at 100° with or without the addition of AIBN.

Registry No.—Thiophenol, 108-98-5; *p*-bromoaniline, 106-40-1; *p*-iodoaniline, 540-37-4; *o*-bromoaniline, 615-36-1; *p*-chloroaniline, 106-47-8; *p*-iodonitrobenzene 636-98-6; iodobenzene, 591-50-4.

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The Addition of *tert*-Butyl Hypochlorite to Isocyanates[1]

J. H. Boyer* and P. P. Fu

Department of Chemistry, University of Illinois, Chicago Circle Campus, Chicago, Illinois 60680

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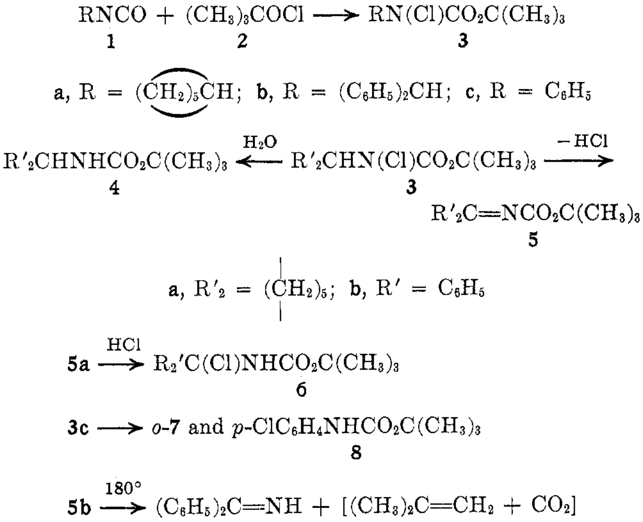
Addition of *tert*-butyl hypochlorite (**2**) to an isocyanate (**1**) gives an unisolated *N*-chlorocarbamate (**3**). Previously known adducts required insertion of the azomethine linkage of an isocyanate into the single bond between (1) hydrogen and each of many elements; (2) oxygen and certain elements, *e.g.*, titanium, tin, and carbon (the reactive ether linkage in orthoformates, formaldehyde acetals, and epoxides); (3) silicon and nitrogen; (4) boron and sulfur; and (5) phosphorus and chlorine.[2] The present work is terminal and grew out of a continuing study of the relationship between an *N*-acylimine and the isomeric isocyanate, $R_2C{=}NC({=}O)Z$ and $R_2C(Z)N{=}C{=}O$.

Under mild conditions the hypochlorite **2** combined with cyclohexyl, benzhydryl, and phenyl isocyanates (**1a–c**). An assumed initial formation of an undetected *N*-chlorocarbamate (**3**) provided an explanation for each product formation. From **3a** hydrolysis during work-up produced *N*-cyclohexylcarbamate (**4a**) and dehydrochlorination to a small extent gave the *N*-*tert*-butoxycarbonylimine (**5a**) of cyclohexanone, detected by hydrolysis into *tert*-butyl carbamate and a product (**6**) in low yield which appears to be a hydrogen chloride adduct.[3]

At 70° an adduct obtained from the neat mixture of **2** and benzhydryl isocyanate (**1b**) underwent dehydrochlorination, affording the *N*-*tert*-butoxycarbonylimine (**5b**) of benzophenone in 87% yield. Identification of benzophenone and *tert*-butyl carbamate, obtained upon hydrolysis, confirmed the structure of the imine. In contrast with the thermolysis of the *N*-benzoylimine of benzophenone at 110–115° into benzophenone[4] (and presumably benzonitrile) the ester **5b** was thermally stable under 170°. At 180° it fragmented to give the imine of benzophenone in 57% yield, but the ketone itself was not detected. Presumably carbon dioxide and isobutylene were also formed.

An apparent rearrangement of the *N*-chloro-*N*-phenylcarbamate (**3c**), obtained from **2** and **1c**, gave both *o*- and *p*-chlorophenylcarbamates (**7** and **8**), with the latter in slight predominance.[5] Each was identified by saponification and decarboxylation into the corresponding chloroaniline.



$$\underset{\mathbf{1}}{\mathrm{RNCO}} + \underset{\mathbf{2}}{(\mathrm{CH_3})_3\mathrm{COCl}} \longrightarrow \underset{\mathbf{3}}{\mathrm{RN(Cl)CO_2C(CH_3)_3}}$$

$$\mathbf{a},\ \mathrm{R} = (\mathrm{CH_2})_5\mathrm{CH};\quad \mathbf{b},\ \mathrm{R} = (\mathrm{C_6H_5})_2\mathrm{CH};\quad \mathbf{c},\ \mathrm{R} = \mathrm{C_6H_5}$$

$$\underset{\mathbf{4}}{\mathrm{R'_2CHNHCO_2C(CH_3)_3}} \xleftarrow{\mathrm{H_2O}} \underset{\mathbf{3}}{\mathrm{R'_2CHN(Cl)CO_2C(CH_3)_3}} \xrightarrow{-\mathrm{HCl}} \underset{\mathbf{5}}{\mathrm{R'_2C{=}NCO_2C(CH_3)_3}}$$

$$\mathbf{a},\ \mathrm{R'_2} = (\mathrm{CH_2})_5;\quad \mathbf{b},\ \mathrm{R'} = \mathrm{C_6H_5}$$

$$\mathbf{5a} \xrightarrow{\mathrm{HCl}} \underset{\mathbf{6}}{\mathrm{R_2'C(Cl)NHCO_2C(CH_3)_3}}$$

$$\mathbf{3c} \longrightarrow o\text{-}\mathbf{7} \text{ and } \underset{\mathbf{8}}{p\text{-}\mathrm{ClC_6H_4NHCO_2C(CH_3)_3}}$$

$$\mathbf{5b} \xrightarrow{180^\circ} (\mathrm{C_6H_5})_2\mathrm{C{=}NH} + [(\mathrm{CH_3})_2\mathrm{C{=}CH_2} + \mathrm{CO_2}]$$

Experimental Section

***tert*-Butyl *N*-Cyclohexylcarbamate (4a).**—A mixture of 5.5 g (44.0 mmol) of cyclohexylisocyanate and 5.1 g (47.0 mmol) of *tert*-butyl hypochlorite in 30 ml of petroleum ether (bp 30–60°) was stirred at room temperature for 15 hr in a 50-ml three-necked round-bottom flask equipped with a stream of dry nitrogen, a stirrer, and a condenser with a drying tube. Unreacted isocyanate, detected by ir absorption at 2250 cm^{-1}, disappeared

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[1] Financial support was received from NASA Grant No. NGR 14-012-004.

[2] S. Ozaki, private communication.

[3] A referee suggests an alternative transformation which does not require the assumption that water is available during chromatography: $\mathbf{3} + \mathrm{HCl\ (anhydrous)} \rightarrow \mathbf{4} + \mathrm{Cl_2}$.

[4] R. Ahmed and W. Lwowski, *Tetrahedron Lett.*, 3611 (1969).

[5] Migration of chlorine in *N*-chloroacetanilide gives *o*- (32.5%) and *p*-chloroacetanilide (67.5%) as reported by J. Kennedy, P. Orton and A. E. Bradfield, *J. Chem. Soc.*, 986 (1927). The evidence indicates an intermolecular process: J. March, "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure," McGraw-Hill, New York, N. Y., 1968, p 431.