The Sodium Borohydride Reduction of 2,2,2-Triphenylethylmercuric Chloride

RODERIC P. QUIRK[1]

Department of Chemistry, University of Arkansas,
Fayetteville, Arkansas 72701

Received April 28, 1972

The mechanism of the borohydride reduction of organomercurials is a subject of considerable current interest.[2–5] The formation of radical intermediates in these reductions has been inferred from labeling experiments, observations of loss of stereochemistry, and structural rearrangements; however, a clear distinction between radical-cage and radical-chain processes has not been possible.[4] While investigating the chemistry of 2,2,2-triphenylethyl organometallic derivatives, it was found that alcohols rather than hydrocarbons are the major products from the sodium borohydride reduction of 2,2,2-triphenylethylmercuric chloride (**1**).

The sodium borohydride reduction of **1** in basic aqueous tetrahydrofuran for 1 hr according to the procedure of Brown and Geoghegan[6] (*i.e.*, open to the atmosphere) produced only a 6% yield of the corresponding hydrocarbon 1,1,1-triphenylethane, although elemental mercury was approximately quantitatively deposited (90–100%). The principal product (70%) was found to be the rearranged alcohol, 1,1,2-triphenylethanol. It was considered that this unusual product could have resulted from solvolysis of the mercurial[7] or from oxygen trapping of intermediate radicals. A control experiment involving stirring the mercurial **1** without sodium borohydride in basic aqueous tetrahydrofuran open to the air for 7.5 hr did not produce any detectable amounts of mercury or alcohol products. This experiment also indicates that oxygen-induced decomposition of the mercurial is not competitive with the reduction reaction. The role of oxygen in the course of these reactions was investigated by carrying out the reductions on a vacuum line after careful degassing. The reaction products using degassed solutions are 1,1,1-triphenylethane (8%) and 1,1,2-triphenylethane (92%) in addition to elemental mercury (99%). It is significant that under these conditions no alcoholic products are observed although predominant rearrangement still occurs. If molecular oxygen is introduced into the reaction flask after the degassing cycles, the reaction products are 1,1,1-triphenylethane (13%), 1,1,2-triphenylethane (3%), 1,1,2-triphenylethanol (58%), and 2,2,2-triphenylethanol (19%).

The observation of rearranged products from all the sodium borohydride reductions of **1** is consistent with the free-radical pathways proposed for this reaction.[8] The production of alcohols in the presence of oxygen is also consistent with the formation of intermediate radicals since oxygen is known to be an efficient radical scavenger.[9,10] It is tempting to conclude that the sodium borohydride reduction of organomercurials proceeds *via* a noncage process since the rate of rearrangement of the 2,2,2-triphenylethyl radical (5×10^7 sec^{-1} at 100°)[11,12] would be expected to be several orders of magnitude slower than diffusion-controlled rates at room temperature.[13] However, since the alcoholic products from the sodium borohydride reduction of **1** are rather anomalous, it is not certain that these conclusions are applicable to other systems.

In contrast to the sodium borohydride reduction, the reduction of **1** with either lithium aluminum hydride or sodium bis(2-methoxyethoxy)aluminum hydride in tetrahydrofuran under an argon atmosphere produced only the unrearranged hydrocarbon, 1,1,1-triphenylethane, in 92%–98% yields. Similarly, reduction of **1** with sodium amalgam in aqueous methanol under argon produced only 1,1,1-triphenylethane in 99% yield. Neither rearranged hydrocarbon nor oxidation products could be detected by vpc analyses of these reaction mixtures. Therefore, these reagents would seem to be preferrable to sodium borohydride for reduction of organomercurials since intermediate radicals apparently are not involved.

Experimental Section

Melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected. Nmr spectra were obtained on dilute solutions using a Varian Model A-60 spectrometer and TMS as an internal standard. The ir spectra were obtained using a Perkin-Elmer Model 337 grating spectrophotometer. Vpc measurements were conducted with a Varian-Aerograph Model 90-P using the internal standard method for quantitative analyses. Hydrocarbon products were separated using a 13-ft, 5% Apiezon L on Chromosorb W column at 200°; the alcohols were analyzed using a 4-ft, 3% Carbowax 20M on Chromosorb G column at 210°. Combustion analyses were performed by Alfred Bernhardt Mikroanalytische Laboratorium, 5251 Elbach über Engelskirchen, West Germany. The yields of elemental mercury were determined by direct weighing of samples after careful washing with water, acetone, and diethyl ether followed by drying.

2,2,2-Triphenylethylmercuric Chloride (1).—A solution of 2,2,2-triphenylethyllithium was prepared from chloro-2,2,2-triphenylethane and lithium ribbon in freshly distilled tetrahydrofuran at −70° according to the procedure of Grovenstein and Williams.[14] The lithium reagent was quenched at −70° with mercuric chloride in diethyl ether to afford after recrystallization from ethanol–benzene a 42% yield of **1** as colorless crystals: mp 196.5–197.5°; nmr (CS_2) δ 7.17 (s, 15), 3.0 (s, 2).

Anal. Calcd for $C_{20}H_{17}HgCl$: C, 48.68; H, 3.47. Found: C, 48.76; H, 3.48.

Reduction of 1 with Sodium Borohydride.—The reduction of **1** with sodium borohydride was carried out employing the procedure of Brown and Geoghehan.[6] The products were recovered

---

[1] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

[2] G. A. Gray, W. R. Jackson, and V. M. A. Chambers, *J. Chem. Soc. C*, 200 (1971).

[3] V. M. A. Chambers, W. R. Jackson, and G. W. Young, *ibid.*, 2075 (1971).

[4] G. M. Whitesides and J. San Filippo, Jr., *J. Amer. Chem. Soc.*, **92**, 6611 (1970).

[5] D. J. Pasto and J. A. Gontarz, *ibid.*, **91**, 719 (1969).

[6] H. C. Brown and P. Geoghegan, Jr., *ibid.*, **89**, 1522 (1967).

[7] R. J. Ouellette, R. Papa, M. Attea, and C. Levin, *ibid.*, **92**, 4893 (1970).

[8] Whitesides and San Filippo[4] have proposed that alkylmercuric hydrides are intermediates in the sodium borohydride reduction of alkylmercuric halides. However, as a referee has pointed out, the intermediacy of a labile organoborane is also possible in these systems.

[9] R. R. Baker, R. R. Baldwin, and R. W. Walker, *Chem. Commun.*, 1382 (1969).

[10] P. D. Bartlett, R. E. Pincock, J. H. Rolston, W. G. Schindel, and L. A. Singer, *J. Amer. Chem. Soc.*, **87**, 2590 (1965).

[11] L. Kaplan, *ibid.*, **88**, 4531 (1966).

[12] D. J. Carlsson and K. U. Ingold, *ibid.*, **90**, 7047 (1968).

[13] A. M. North, *Quart. Rev. Chem. Soc.*, **20**, 421 (1966).

[14] E. Grovenstein, Jr., and L. P. Williams, Jr., *J. Amer. Chem. Soc.*, **83**, 412 (1961).

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$_2$SO$_4$, 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

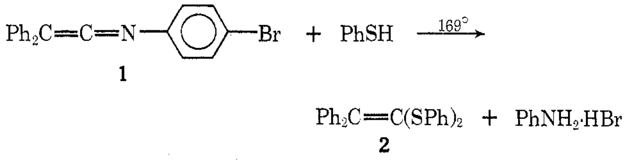
Marvin W. Barker,* Susan C. Lauderdale,[1a] and Joseph R. West[1b]

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

Received March 16, 1972

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.

---

[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.