Reaction of Benzylmagnesium Chloride with Formaldehyde

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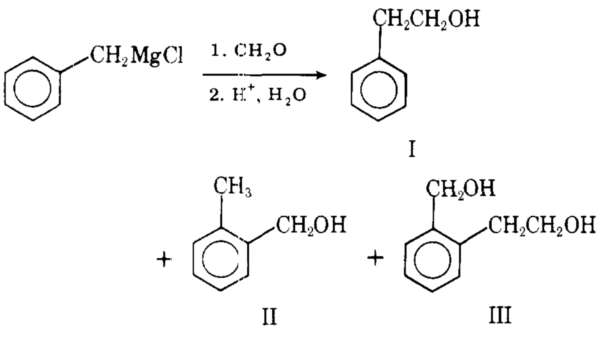
The reaction of benzylmagnesium chloride with both monomeric formaldehyde and paraformaldehyde has been studied by varying the concentration of the aldehyde systematically. The three principal products of the reaction with monomeric formaldehyde are 2-phenylethanol, *o*-tolylcarbinol, and *o*-(2-hydroxyethyl)benzyl alcohol. 2-Phenylethanol is a minor product and is relatively insensitive to concentration changes. The major products, *o*-tolylcarbinol and *o*-(2-hydroxyethyl)benzyl alcohol, are extremely concentration dependent. At low aldehyde concentrations, *o*-tolylcarbinol predominates, but at high aldehyde concentrations this product virtually disappears in favor of *o*-(2-hydroxyethyl)benzyl alcohol. With paraformaldehyde, *o*-tolylcarbinol is always the major product regardless of concentrations. Only small amounts of *o*-(2-hydroxyethyl)benzyl alcohol are even formed and then only at very high aldehyde concentrations. The latter results would indicate that the polymer itself does not react directly but serves to supply a steady but low concentration of reactive monomer, a situation which disfavors formation of *o*-(2-hydroxyethyl)benzyl alcohol. The intermediate leading to the latter product was trapped by trimethylchlorosilane and characterized. Despite many conflicting and erroneous reports in previous literature and textbooks, the formaldehyde reaction with benzylmagnesium chloride is not a paradox but has many features in common with other aldehyde–benzyl Grignard reactions.

Our laboratory has been engaged for some time in a detailed investigation of allylic and benzylic types of organometallics. There has been a hiatus in our work on the benzylic systems, since it seems that our earlier disclosures[1] should have dispelled many of the prior contradictions that had existed in this area. In 1967 we reported[2] that even the classic reaction of benzylmagnesium chloride with formaldehyde did not constitute an exceptional case, in that the products were concentration dependent and similar in all respects to the higher aldehydes in this series. Apparently this latter disclosure has been overlooked since incorrect and confusing statements are still being published in journals[3] and modern textbooks.[4]

It is the purpose of this paper to describe in detail our findings concerning the reaction between benzylmagnesium chloride and both gaseous and polymeric formaldehyde (paraformaldehyde). Hopefully this will curtail future inaccuracies concerning this case from finding their way into the chemical literature.

The reaction of benzylmagnesium chloride and paraformaldehyde was first reported by Grignard[5] in 1903 who claimed that the product was 2-phenylethanol (I). In the same year, this was contradicted by other workers[6] who stated that actually the product was the abnormal alcohol, *o*-tolylcarbinol (II). In 1948 it was claimed[7] that 2-phenylethanol resulted when gaseous formaldehyde was treated with benzylmagnesium chloride. Some years later another report[8] claimed that only *o*-tolylcarbinol formed when gaseous formaldehyde was used. All of this early work was hampered by the lack of sensitive analytical methods which undoubtedly contributed to the contradictory results and hence should not be judged too harshly.



(1)

In the first paper[1a] of this series, we were able to show that both acetaldehyde and trifluoroacetaldehyde reacted with benzylmagnesium chloride to give products structurally similar to I, II, and III above (eq 1) and that all the reactions were concentration dependent. It will be shown that the results (eq 1) with formaldehyde are virtually the same.

Results and Discussion

Table I lists the results obtained when the concentration of benzylmagnesium chloride was held constant (0.4 M throughout) and the number of grams of gaseous formaldehyde introduced into the system was increased from 4 to 28. Significantly, compounds I, II, and III were found in every case. The amount of 2-phenylethanol (I) produced was influenced least by the concentration changes of the formaldehyde. It increased by a factor of only 1.5 while the formaldehyde increased from 4 to 28 g. It is interesting that the amount of *o*-tolylcarbinol produced was related inversely to the amount of formaldehyde used. At low aldehyde concentrations, *o*-tolylcarbinol was the principal product, but at high aldehyde concentrations it virtually disappeared. This was exactly opposite to the behavior of compound III which was the major product at high aldehyde concentrations.

Table II lists the results when the concentration of the benzylmagnesium chloride was again held constant at 0.4 M (except for entry 13) but paraformaldehyde was used throughout. The amount of 2-phenylethanol again gradually increased with aldehyde concentration. In this case, however, the *o*-tolylcarbinol increased substantially as the aldehyde concentration increased, such that it was the major product in every case. The amount of diol (III) did not show the dramatic increase as in the case with gaseous formaldehyde. It is our contention that the paraformaldehyde polymer, which is only sparingly soluble in diethyl ether, breaks down to provide a steady but low concentration of monomeric formaldehyde which is the reactive species. At no time is the concentration of monomer high and hence little diol (III) is ever produced. When the concentration of the Grignard was increased (entry 13), only the amount of *o*-tolylcarbinol was increased substantially.

While the mechanism for the reaction of benzyl organometallics with carbonyl compounds has never been established with certainty, we have found the earlier suggestions[9] rather attractive since they do offer an explanation for the products of such reactions with carbonyl compounds. This paper indicates that the earlier proposals[9] accommodate the formaldehyde results as well.

A slight extension of the Young–Siegel version[9b] of such reactions would predict that species like IV or V should exist

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Table I. Concentration Effects in Reaction of Benzylmagnesium Chloride[a] and Gaseous Formaldehyde

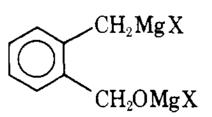
	CH_2O		mole ratio	g of products		
	g	mol	$CH_2O/PhCH_2MgCl/g$	2-phenylethanol (I)	*o*-tolylcarbinol (II)	*o*-(2-hydroxymethyl)-benzyl alcohol (III)
(1)	4.0	0.133	0.444	0.80	7.3	0.9
(2)	5.5	0.183	0.612	0.72	8.0	1.45
(3)	8.0	0.266	0.888	1.06	8.7	6.8
(4)	9.5	0.316	1.05	1.24	4.4	8.5
(5)	15.5	0.516	1.72	1.30	1.9	16.1
(6)	15.5	0.516	1.72	1.31	1.4	17.9
(7)	20.5	0.683	2.28	1.31	1.1	22.0
(8)	21.5	0.716	2.39	1.37	1.1	16.8
(9)	26.8	0.893	2.98	1.05	0.5	19.4
(10)	28.0	0.933	3.10	1.19	0.2	23.1

[a] In every case, 0.3 mol of benzylmagnesium chloride at an initial concentration of 0.4 M was used.

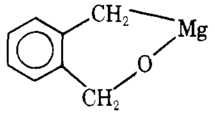
Table II. Concentration Effects in Reaction of Benzylmagnesium Chloride[a] and Paraformaldehyde[b]

	$H(CH_2O)_xOH$		mol ratio	g of products		
	g	mol[a]	$H(CH_2O)_xOH/PhCH_2MgCl/g$	2-phenyl ethanol (I)	*o*-tolyl carbinol (II)	*o*-(2-hydroxyethyl)-benzyl alcohol (III)
(1)	3.0	0.1	0.333	0.60	7.2	
(2)	3.0	0.1	0.333	0.44	5.8	
(3)	6.0	0.2	0.667	0.96	14.6	
(4)	6.0	0.2	0.667	0.98	14.3	
(5)	9.0	0.3	1.00	1.17	16.7	trace
(6)	9.0	0.3	1.00	1.07	14.7	trace
(7)	18.0	0.6	2.0	1.31	15.6	2.9
(8)	18.0	0.6	2.0	1.33	15.0	4.3
(9)	27.0	0.9	3.0	1.36	16.1	2.4
(10)	27.0	0.9	3.0	1.43	15.4	2.6
(11)	36.0	1.2	4.0	1.53	15.8	4.0
(12)	36.0	1.2	4.0	1.47	15.8	4.5
(13)[c]	36.0	1.2	3.0	2.7	24.7	3.5

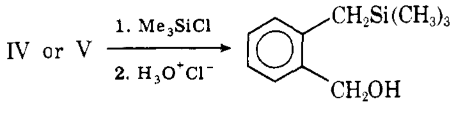
[a] The moles were calculated using a mol wt of 30 for CH_2O. [b] The initial concentration of benzylmagnesium chloride was always 0.4 M in a volume so as to contain 0.30 mol except for entry 13. [c] The initial concentration was 1.6 M in this case.



IV



V



VI (2)

in solution at some point. Clearly formulations such as IV and V are oversimplifications. Not only would the Schlenk equilibrium be involved with these species, but their degree of aggregation would be concentration[10] and solvent[11] dependent. Furthermore their Mg atoms would be complexed with solvent and/or carbonyl species. Sufficient data are not at hand to assess the importance of the interplay of all the variables involved in such systems and hence a detailed mechanism cannot be written. Suffice it to say, acid hydrolysis of either IV or V would produce *o*-tolylcarbinol, while formaldehyde should react with either species to form *o*-(2-hydroxyethyl)benzyl alcohol[12] (III). Hence, whether *o*-tolylcarbinol or diol III is the predominant product should, at least in part, be a function of the formaldehyde concentration. By postulating the existence of species like IV and/or V, the results obtained in Tables I and II can be explained nicely. Furthermore, it would be predicted that when the mole ratio of formaldehyde/benzyl Grignard reagent is less than 1, the concentrations of IV and V should be maximized. It should be possible in such cases to intercept IV and/or V by adding an anion trap like trimethylchlorosilane prior to hydrolysis of the reaction mixture. Such experiments were carried out with both gaseous[13] formaldehyde and paraformaldehyde. In both cases, *o*-(hydroxymethyl)benzyltrimethylsilane (VI) was isolated, but no *o*-(2-hydroxyethyl)benzyl alcohol (III). The formation of VI strongly points to the presence of an organometallic intermediate which should be capable of reacting with more formaldehyde[14] to form III. This would explain the increase in diol III as the formaldehyde concentration was increased.

$$\text{IV or V} \xrightarrow[\text{2. } H_3O^+Cl^-]{\text{1. } CH_2O} \text{III} \qquad (3)$$

Experimental Section

Benzylmagnesium Chloride. This was prepared in essential accordance with the directions published previously.[1b] In every case the benzylmagnesium chloride was prepared at about 1.67 M and then diluted to provide the desired concentration.

Monomeric Gaseous Formaldehyde.[13] In a 200-mL one-neck flask was placed 25 g of paraformaldehyde which had been dried for several days in a desiccator over P_2O_5. The system was flushed with dry N_2 and also flamed out to eliminate any moisture. A glass tube which joined the flask to a receiver (a 12 in. test tube with a ground glass joint) was wrapped with heating tape to keep the gaseous formaldehyde from repolymerizing as it formed. The test tube receiver was immersed in a dry ice–isopropyl alcohol bath. The paraformaldehyde was heated with an oil bath to 190–200 °C. The gaseous formaldehyde which formed condensed in the cold test tube. Some repolymerization would often occur in the glass connecting tube despite the heating tape but usually the depolymerization would be complete (1–1.5 h) before the tube became blocked. The liquid formaldehyde was clear and colorless but sometimes contained a white precipitate. It was kept in the dry ice bath until ready for use, protected from moisture with a "Drierite" filled drying tube.

***o*-(2-Hydroxyethyl)benzyl Alcohol.**[12] This compound was prepared in 59% yield by reduction of homophthalic acid with $LiAlH_4$ using the technique[15] for ether insoluble acids. The $LiAlH_4$ slurry was refluxed for 144 h and then cooled in an ice bath for 0.5 h. Distilled water was then added and the mixture was stirred for several hours at room temperature. The mixture was allowed to settle and the ether solution was decanted. The aqueous layer was filtered and the precipitate washed with diethyl ether. The ether solutions were combined and dried over anhydrous K_2CO_3. Ether removal left a pale yellow liquid which was distilled. There was obtained 6.7 g of *o*-(2-hydroxyethyl)benzyl alcohol: bp 154 °C (1.7 mm); NMR ($CDCl_3$) δ 2.73 (t, 2, CH_2), 3.60 (t, 2, CH_2), 4.20 (s, 2, OH), 4.42 (s, 2, CH_2), 7.1 (m, 4, aromatic).

Anal. Calcd for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 71.04; H, 8.07.

***o*-(Hydroxymethyl)benzyltrimethylsilane.** The Grignard reagent of *o*-chlorobenzyltrimethylsilane[16] was prepared in refluxing THF from 5.0 g (0.2 g-atom) of "activated" Mg powder[17] and 20.0 g (0.1 mol) of the chloride. The mixture was refluxed for 10 h and then a few drops of ethyl bromide were added whereupon it was refluxed for 24 h. To the resulting black slurry was added 6.0 g (0.2 mol) of paraformaldehyde and the mixture was refluxed 24 h. Ethyl ether (50 mL) was then added followed by immediate hydrolysis with 15% HCl solution. The ethereal solution (following the usual workup) was dried over anhydrous K_2CO_3. After solvent removal, the residue was distilled giving 5.2 g, bp 83–85 °C (0.35 mm), of a yellow liquid. Analysis by VPC (5 ft × 0.25 in. stainless steel column packed with 5% FFAP on 60–80 mesh, AW/DMCS treated Chromosorb G at 160 °C) showed it to be a mixture of several components. Column chromatography on alumina was employed with petroleum ether (65–7 °C) to elute the impurities followed by ethyl ether which eluted *o*-(hydroxymethyl)-benzyltrimethylsilane. An infrared and NMR spectrum were consistent with this structure.

Anal. Calcd for $C_{11}H_{18}OSi$: C, 67.98; H, 9.34. Found: C, 67.82; H, 9.47.

Benzylmagnesium Chloride and Gaseous Monomeric Formaldehyde. All reactions listed in Table I were carried out in a similar manner. The procedure described below for entry 10, Table I, is typical for all runs.

A 0.4 M solution of benzylmagnesium chloride in ethyl ether was prepared (see above) in a dry, 2-L flask equipped with a ground glass stirrer and dry ice condenser. In this case, 180 mL (0.3 mol) of the original Grignard solution was diluted to a volume of 750 mL with anhydrous ethyl ether to obtain the 0.4 M solution. A dry, 8-mm, glass tube was connected to the test tube containing the liquid formaldehyde prepared (see above) from 50 g of paraformaldehyde. After the addition tube and test tube were weighed, the former was connected to the flask containing the Grignard solution. The liquid formaldehyde was allowed to vaporize at room temperature and the vapors were introduced *over* the stirred Grignard solution to avoid plugging of the addition tube. This required 45 min, whereupon the solution was stirred an additional 1 h at room temperature. The addition tube and test tube were then reweighed and the weight of formaldehyde used determined by difference (26.8 g, 0.895 mol). This mixture was hydrolyzed with 100 mL of saturated NH_4Cl solution followed by the addition of 100 mL of water. The mixture was stirred for 0.5 h and then filtered. The aqueous layer was washed 3× with 75-mL portions of ethyl ether. The combined ether extracts were dried over anhydrous K_2CO_3.

The solvent was removed by distillation directly from the K_2CO_3 using a 12 in. Vigreux column. The residue was also distilled directly from the K_2CO_3 but at reduced pressure. The following fractions were obtained: (a) 3.7 g, bp 40–45 °C (3.0 mm), (d) 20.5 g, bp 155–164 °C (1.0–2.0 mm). A small amount of dark brown residue remained in the distillation flask.

All fractions were analyzed by VPC (F and M Model 500 chromatograph with a glass liner in the injection port). Fraction (a) proved to be toluene (5 ft × 0.25 in. stainless steel column packed with 10% DEGS on 60–80 mesh Chromosorb W at 145 °C). The ethyl ether distillate was also found to contain some toluene. Fraction (b) (same column as above) contained benzyl alcohol, 2-phenylethanol, *o*-tolylcarbinol, and bibenzyl (elution in that order). Samples of each of these four compounds were collected by VPC (same column as above) and their identity established by matching their IR spectra with those of authentic samples. Fraction (c) (5 ft × 0.25 in. stainless steel column packed with 5% FFAP on 60–80 mesh, AW/DMCS treated Chromosorb G at 225 °C)[18] contained a mixture of the products in fraction (b) and an unknown component with the same retention time as *o*-(2-hydroxyethyl)benzyl alcohol. With this same column,[18] fraction (d) contained only one component with the same retention time and IR as that of an authentic sample of *o*-(2-hydroxyethyl)benzyl alcohol (vide supra). Further confirmation of the identity of this product was achieved by converting 5 g of fraction (d) to its bis(*p*-nitrobenzoate) ester with *p*-nitrobenzoyl chloride. A white solid was obtained melting at 131.5–134 °C. IR and melting point were identical to that of an authentic sample.

Benzylmagnesium chloride (always 0.4 M in Et_2O) was treated with varying amounts of gaseous formaldehyde. Table I shows the effect of aldehyde concentration on the course of the reaction.

Benzylmagnesium Chloride and Paraformaldehyde. All reactions listed in Table II were carried out in a similar fashion. The directions given below for entry 10 in Table II are typical for all the runs listed.

A mixture of 27 g (0.9 mol) of paraformaldehyde (dried for several days in a desiccator over P_2O_5) and 500 mL of anhydrous diethyl ether was placed in a dry flask (2 L) equipped with a ground glass stirrer and reflux condenser fitted with a "Drierite" drying tube. To this slurry (under dry N_2) was added 0.3 mol of benzylmagnesium chloride contained in 185 mL of solution. The total volume was then increased to 750 mL by adding an additional 65 mL of anhydrous ethyl ether. The result was a 0.4 M Grignard solution. The mixture was stirred for 24 h at room temperature.

Hydrolysis was effected with 100 mL of saturated NH_4Cl solution followed by the addition of 100 mL of water. The mixture was stirred for 1 h and filtered and the filtrate was separated into layers. The aqueous layer was washed 3× with 75-mL portions of diethyl ether. The ether extracts were combined and dried over anhydrous K_2CO_3. The ether was removed by distillation through a 12 in. Vigreux column and the residue was distilled to give the following fractions: (a) 2.0 g, bp 48 °C (100 mm); (b) 19.2 g, bp 60–120 °C (1 mm); (c) 2.8 g, bp 120–140 °C (1 mm); (d) 4.4 g, bp 140–175 °C (1 mm). All analyses were done by VPC using the same columns described previously for the gaseous formaldehyde products. Fraction (a) was principally toluene. Fraction (b) was a mixture of benzyl alcohol, 2-phenylethanol, *o*-tolylcarbinol, and bibenzyl. The identity of all of these was confirmed by VPC collection and matching their IR spectra with authentic samples. *o*-Tolylcarbinol was the major component in fraction (b).

Table II illustrates the effects of changes in concentration of paraformaldehyde on the course of this reaction.

Benzylmagnesium Chloride and Gaseous Formaldehyde. Addition of Trimethylchlorosilane. To a solution containing 0.3 mol of $C_6H_5CH_2MgCl$ in 750 mL of ethyl ether was added 4.2 g (0.14 mol) of gaseous formaldehyde over a 15-min period. The mixture was stirred for 1 h at room temperature and then 65.4 g (0.6 mol) of freshly distilled trimethylchlorosilane was added. The resulting solution was then stirred for 24 h at room temperature.

The workup and analysis by VPC was similar to that described above for the reaction of the benzyl Grignard with gaseous formaldehyde alone. The results of the analysis were: (a) 25.2 g of benzyltrimethylsilane, (b) 0.2 g of 2-phenylethanol, (c) 2.6 g of *o*-tolylcarbinol, and (d) 2.3 g of *o*-(hydroxymethyl)benzyltrimethylsilane. No *o*-(2-hydroxyethyl)benzyl alcohol was found.

When the above reaction was repeated using paraformaldehyde, *o*-(hydroxymethyl)benzyltrimethylsilane was again found in the products but no *o*-(2-hydroxyethyl)benzyl alcohol.

Registry No.—*o*-(2-Hydroxyethyl)benzyl alcohol, 6346-00-5; 2-phenylethanol, 60-12-8; *o*-tolylcarbinol, 89-95-2; *o*-chlorobenzyltrimethylsilane, 68307-67-5; benzyl chloride, 100-44-7; homophthalic acid, 89-51-0; *o*-(hydroxymethyl)benzyltrimethylsilane, 57754-01-5; trimethylchlorosilane, 75-77-4; benzyltrimethylsilane, 770-09-2; formaldehyde, 50-00-0; paraformaldehyde, 30525-89-4.

References and Notes

(1) (a) R. A. Benkeser and T. E. Johnston, *J. Am. Chem. Soc.*, **88**, 2220 (1966); (b) R. A. Benkeser and W. DeTalvo, *ibid.*, **89**, 2141 (1967); (c) R. A. Benkeser, T. E. Johnston, and W.-H. Tong, *J. Org. Chem.*, **33**, 2203 (1968).

(2) R. A. Benkeser and W. DeTalvo, Abstracts, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1967, Paper No. 62.

(3) S. Nunomoto and Y. Yamashita, *J. Chem. Soc. Jpn. Ind. Chem. Sect.*, **73**, 1990 (1970). These authors claim that with a mole ratio of benzyl Grignard–gaseous formaldehyde of 1:1 a quantitative yield of *o*-tolylcarbinol is realized. Furthermore, they maintain that with formaldehyde, no significant change was observed by varying the aldehyde concentration. They also state that "intuitively" one might expect that intermediates like IV and V (see above) would react with another molecule of formaldehyde but "this

is not the case". Finally, they do not report carrying out any reactions with paraformaldehyde itself.
(4) See T. W. G. Solomons in "Organic Chemistry", Wiley, New York, 1976, p 592, where it is suggested that 2-phenylethanol be made by treating formaldehyde with benzylmagnesium bromide.
(5) V. Grignard, *Bull. Soc. Chim. Fr.*, **29**, 953 (1903).
(6) M. Tiffeneau and R. DeLange, *C. R. Hebd. Seances Acad. Sci.*, **137**, 573 (1903).
(7) M. Mousseron and N. P. Du, *Bull. Soc. Chim. Fr.*, **[5] 15**, 91 (1948).
(8) S. Siegel, W. M. Boyer, and R. R. Jay, *J. Am. Chem. Soc.*, **73**, 3237 (1951).
(9) (a) J. R. Johnson, *J. Am. Chem. Soc.*, **55**, 3029 (1933); (b) See W. G. Young and S. Siegel, *ibid.*, **66**, 354 (1944); (c) for a modified version see ref 8.
(10) E. C. Ashby and W. E. Becker, *J. Am. Chem. Soc.*, **85**, 118 (1963).
(11) E. C. Ashby and M. B. Smith, *J. Am. Chem. Soc.*, **86**, 4363 (1964).
(12) S. Siegel and S. Coburn, *J. Am. Chem. Soc.*, **73**, 5494 (1951).
(13) J. F. Walker, "Formaldehyde", Reinhold Publishing Corp., New York, 1964, p 46.
(14) It should be noted (ref 3) that Nunomoto and Yamashita claim that intermediates like IV or V did not react with more formaldehyde as one might expect. They were forced to this conclusion because they observed no *o*-(2-hydroxyethyl)benzyl alcohol. They *do* claim, however, that IV and V react with trimethylchlorosilane.
(15) R. F. Nystrom and W. G. Brown, *J. Am. Chem. Soc.*, **69**, 1197 (1947).
(16) C. Eaborn and S. H. Parker, *J. Chem. Soc.*, 939 (1954).
(17) M. Kharasch and O. Reinmuth, "Grignard Reactions of Non-Metallic Substances", Prentice-Hall, New York, 1954, pp 8 and 9.
(18) Analysis of *o*-(2-hydroxyethyl)benzyl alcohol by VPC was difficult because of the ease of dehydration to isochroman and also oxidation to the aldehyde. It could be done, however, using the column indicated and a flow rate of 90 mL/min. A glass liner in the injection port of the instrument was necessary to prevent dehydration.

Reduction of Organomercurials by Sodium Dithionite

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The reaction between organomercuric salts and sodium dithionite was examined under various conditions. Several reactions occur, depending on the organofunctional classification of the mercurial. For simple hydrocarbon alkyls, one-electron reduction (probably involving the radical anion $\cdot SO_2^-$) is the predominant reaction, producing alkyl radicals and resulting in complete loss of any net enantiomeric (but not necessarily diastereomeric) resolution possessed by prochiral substrates. Aryl substrates undergo dithionite-induced symmetrization, and products of oxymercuration of simple alkenes undergo dithionite-induced reversion to the olefin. In both of the latter reactions, the free mercury(II) generated is rapidly reduced, although initially the role of dithionite is only that of any strong ligand.

Aqueous dithionite is an effective reducing agent of cobalt(III) and manganese(III) porphyrins[1] and alkylcobalt(III) chelates[2] (in-plane ligand = corrin, $(dmgH)_2$, and $(dpgH)_2$). The question of outer- or inner-sphere nature of the reduction has not been unambiguously established,[3] but an observed half-order dependence[4] of the rate on dithionite concentration has led to the hypothesis of rate-limiting *one*-electron reduction by the radical anion $\cdot SO_2^-$, formed via a dissociative equilibrium (eq 1).[5]

$$S_2O_4^{2-} \rightleftharpoons 2\,\cdot SO_2^- \qquad K(H_2O, 25\ °C) = 1.6 \times 10^{-10} \tag{1}$$

Recently, Todhunter and Currell[6] reported that organomercuric salts (but not diorganomercurials) could be reduced, viz., "symmetrized", by dithionite in ethanol, according to the stoichiometry shown in eq 2.

$$2RHgX + S_2O_4^{2-} \rightarrow RHgR + Hg^0 + 2Cl^- + 2SO_2 \tag{2}$$

These workers reported results only for one aromatic substrate (*p*-chloromercuribenzoic acid) and one aliphatic substrate (*exo-cis*-3-hydroxy-2-norbornylmercuric chloride). In the former case, styrene added to the initial solution was recovered from the reaction unchanged. In the latter case, the dialkylmercurial product was obtained with complete retention of configuration at both C–Hg centers. Consistent with these findings, Todhunter and Currell proposed a *two*-electron reduction mechanism (eq 3–5), in analogy to that proposed for magnesium metal induced "symmetrization".[7]

$$RHgX + 2e^- \longrightarrow RHg^- + X^- \tag{3}$$

$$RHg^- + RHgX \longrightarrow RHgHg + X^- \tag{4}$$

$$RHgHgR \longrightarrow \left[\begin{array}{c} RHgR \\ | \\ Hg \end{array}\right] \longrightarrow RHgR + Hg^0 \tag{5}$$

The magnesium reaction[7] is presently the only established method for converting chiral *hydrocarbon* alkylmercuric salts (e.g., (+)- or (−)-*sec*-butylmercuric bromide) as well as oxymercurated materials to the corresponding dialkylmercurials with complete retention of configuration at carbon. Thus, it was of interest to see if the scope of the dithionite reduction could be conveniently extended to include hydrocarbon alkylmercuric salts, and if so, whether or not the products obtained possess fully retained stereochemistry (thereby supporting the proposed two-electron reduction).

In contrast to the result obtained with the oxymercurial utilized by Todhunter and Currell,[6] we have found that hydrocarbon alkylmercuric halides (e.g., *n*-BuHgBr, *s*-BuHgBr, and cyclohexylmercuric bromide) are essentially inert to the prescribed reaction conditions (absolute ethanol, room temperature, under nitrogen or open to the air). However, it was found that the utilization of more suitable reaction conditions would allow reduction to take place. The selection of these conditions was based on several factors.

(i) Although ethanol is a reasonable compromise between the aqueous high solubility of $Na_2S_2O_4$ and the organic solubility of mercurials, the reaction system remained heterogeneous. Homogeneity would probably aid the reduction.

(ii) Prior coordination of the reductant to mercury is expected to facilitate reduction via an inner-sphere process. Alkylmercuric halides are covalent compounds wherein the mercury center possesses some, but not large, residual coordinating capacity. On the other hand, organomercuric salts with weak ligand anions (e.g., acetate and nitrate) are ionized or have substantial ionic character, such that the mercury center has a pronounced Lewis acidity, thus promoting coordination and reduction. Reduction might also be facilitated by an aprotic solvent, wherein an anionic reductant, e.g., $S_2O_4^{2-}$, will lack solvation via hydrogen bonding and thus will have a much greater tendency to coordinate to mercury.

(iii) The reducing potential of dithionite is greatly enhanced in basic media (eq 6 and 7).[6]

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