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The Hydride Transfer Nature of the Reduction of Carbonium Ions by HBr, HI and a Pt and an Ir Hydride[1]

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HBr in sulfuric acid solutions instantly reduces carbonium ions with pK_R^+ more negative than -11 and fails to reduce carbonium ions with pK_R^+ more positive than -11. This is true for carbonium ions that equilibrate with either alcohols or olefins. The success of HI reductions and Br_2 oxidations are also a function of the pK_R^+ of the carbonium ion reduced or produced. In reductions with $PtHCl[P(C_2H_5)_3]_2$ and $IrH_2Cl[P(C_2H_5)_2(C_6)_5]_3$, the pK_R^+ value is not so easily defined because the reactions become increasingly slow near the limiting pK_R^+ value. The existence of these limiting pK_R^+ values indicates the hydride transfer nature of these reactions. The hydrocarbons produced by the reductions were isolated in several instances.

Hydride transfer reactions are characterized by the transfer of H with a pair of electrons between two Lewis acids. It is a remarkable fact that such reactions are conducted in protonic solvents including aqueous mineral acids where free hydride ions would be instantly converted to molecular hydrogen.[3] Two groups have shown that log k for a hydride transfer reaction is directly proportional to the difference in pK_R^+ of the two carbonium ions exchanging the hydride moiety, providing steric effects are constant.[4] A second characteristic is the thermodynamic necessity that the direction of hydride transfer will be a function of the stability (pK_R^+) of the carbonium ions. With this background, the reduction of carbonium ions by HBr was investigated.[5]

HBr Reductions.—The data in Table I demonstrate that reduction (or non-reduction) of a carbonium ion by HBr is a function of the pK_R^+ value[6] (for carbonium ions in equilibrium with alcohols) or the $pK'_R{}^+$ value[7] (for carbonium ions in equilibrium with olefins). The demarcation line for either pK_R^+ or $pK_R'^+$ is -11. Carbonium ions with more negative values are reduced and those with more positive values are inert. The reductions are dramatic, the red color of the carbonium ion solution turning completely colorless within a second after the addition of a small amount of powdered NaBr. The rapidity of these reductions allows their easy identification without interference from the slow oxidation of HBr to Br_2. The rapidity also shows that HBr, as expected, is a hydride donor of exceptionally small steric requirements.[4]

The H_2SO_4 concentration also affects the reduction. HBr in 75% H_2SO_4 is a somewhat stronger reducing agent than HBr in 96% H_2SO_4 as shown in Table I. It is suspected that this decrease in reducing potential is related to an increase in the free energy of the Br^+ produced in the equation

$$\mathrm{R^+ + HBr = (R{-}H{-}Br)^+ = RH + Br^+} \xrightarrow{\mathrm{Br^-\ or\ HBr}} \mathrm{Br_2} \qquad (1)$$

In the higher acidity, the decrease in Br^- activity diminishes the energy of formation of Br_2 from Br^+ and Br^-. This interpretation is in accord with qualitative estimates from ultraviolet spectra of the HBr/Br^- equilibrium which indicated that HBr and Br^- concentrations are equal in the neighborhood of 70% H_2SO_4.

It has been tacitly assumed that the reduction can be represented by eq. 1, principally because there is little other alternative. The hydrocarbon RH has been isolated in over 90% yield in the specific case of 4,4′,4′′-trinitrotriphenylmethane. The reduction of diphenylmethyl cation produced principally monobrominated diphenylmethane,[8] in which the bromine probably is attached to the phenyl ring.

Br_2 Oxidations.—The results with HBr reductions suggested that the reverse reaction, Br_2 oxidation, should also be a hydride transfer process.

$$\mathrm{RH + Br_2 = (R{-}H{-}Br{-}Br) = R^+ + HBr + Br^-}$$

Based on kinetic isotope effects, Swain and Rosenberg[9] reached the same conclusion for the oxidation of secondary alcohols by Br_2.

Using as solvent a 51% solution of P_2O_5 in acetic acid, triphenylmethane (pK_R^+ of cation -6.63) and 4,4′,4′′-trimethoxytriphenylmethane (pK_R^+ of cation 0.82) were oxidized to their corresponding arylmethyl cations. 4-Nitrotriphenylmethane (pK_R^+ -9.15) and diphenylmethane (pK_R^+ -13.3) were not oxidized. The dividing line (pK_R^+ of about -8) was not identical to that for HBr reductions because the conditions were somewhat different.

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[2] Research participant in the National Science Foundation program for college chemistry teachers.

[3] For a review, N. Deno, H. Peterson and G. Saines, *Chem. Revs.*, **60**, 7 (1960).

[4] H. Dauben, Jr., and L. M. McDonough, Ph.D. Thesis of L. M., Univ. of Washington, 1960; N. Deno, G. Saines and M. Spangler, *J. Am. Chem. Soc.*, **84**, 3295 (1962).

[5] Singularly, we have been unable to find any reference to such HBr reductions although the present work shows that such reactions are common. The similar HI reductions are well known.

[6] N. Deno, J. Jaruzelski and A. Schriesheim, *J. Am. Chem. Soc.*, **77**, 3044 (1955).

[7] N. Deno, P. Groves, J. Jaruzelski and M. Lugasch, *ibid.*, **82**, 4719 (1960).

[8] Reduction of 20 g. of diphenylmethanol with 28 g. of NaBr in 76% H_2SO_4 gave 14.6 g. (b.p. 160-164°, 3 mm.), 2.7 g. (b.p. 164-192°, 3 mm.), and 4.5 g. of residue. The principal product appears to be monobrominated diphenylmethane from its b.p. In more dilute runs, diphenylmethane (identified by infrared spectra) can be isolated from a HBr or HI reduction of diphenylmethyl cation in polyphosphoric acid containing 70% P_2O_5 and 30% H_2O.

[9] C. G. Swain and A. S. Rosenberg, *J. Am. Chem. Soc.*, **83**, 2154 (1961).

TABLE I

REDUCTION OF ARYLCARBONIUM IONS BY HBr IN SULFURIC ACIDS

		H_2SO_4,[a] %			
Ar_3C^+	pK_R^+	75	81	86	96
4,4′,4″-Trimethoxy	0.82	0	0	0	0
4,4′-Dimethoxy	− 1.24	0	0	0	0
2,2′,2″-Trimethyl	− 3.4	0	0	0	0
4,4′,4″-Trimethyl	− 3.56	0	0	0	0
4-Methyl	− 5.24	0	0	0	0
3,3′,3″-Trimethyl	− 6.35	0	0	0	0
4,4′,4″-Triisopropyl	− 6.54	0	0	0	0
Unsubstituted	− 6.63	0	0	0	0
4-Nitro	− 9.15	0	0	0	0
3,3′,3″-Trichloro	−11.03	[b]	0	0	0
4,4′-Dinitro	−12.90	X	X	X	0
4,4′,4″-Trinitro	−16.27	—	—	—	X
Ar_2CH^+					
4,4-Dimethoxy	− 5.71	0	0	0	0
2,2′,4,4′,6,6′-Hexamethyl	− 6.6	0	0	0	0
4-Methoxy	− 7.9	0	0	0	0
4,4′-Diphenoxy	− 9.85	0	0	0	0
4,4′-Dimethyl	−10.4	0	0	0	0
4-Ethyl	−11.6	—	X	X	0
4-Isopropyl	−11.6	X	0	0	0
4-*t*-Butyl	−11.8	X	X	0	0
4,4′-Di-*t*-butyl	−13.2	—	X	0	0
4,4′-Difluoro	−13.03	X	0	0	0
Unsubstituted	−13.3	X	X	0	0
4,4′-Dichloro	−13.96	X	X	X	0
4,4′-Dibromo	−14.16	—	X	X	0
4,4′-Diiodo	−14.26	—	—	X	0
$Ar_2C^+(CH_3)$					
4,4′-Dimethoxy	− 5.5	0	0	0	0
Unsubstituted	−10.4	0	0	0	0
4,4′-Dichloro	−11.4	—	X	X	0
9-Methyl-9-fluorenyl	−16.60	—	—	—	X
ArC^+R_2					
2-(4′-Methoxyphenyl)-bornyl	− 6.4	0	0	0	0
2-(4′-Methylphenyl)-bornyl	− 8.4	0	0	0	0
2-Phenylbornyl	− 8.8	0	0	0	0
Phenylcyclopentyl	~−10[c]	0	0	0	0
Phenylcyclohexyl	~−11[c]	0	0	0	0
α,α,2,4,6-Pentamethyl-benzyl	−12.2	—	—	X	0
α,α,2,3,4,5,6-Heptamethyl-benzyl	−12.4	—	X	X	X

[a] An "X" signifies instant reduction. A dash signifies that reduction would presumably have taken place but the test was not run because the carbonium ion does not predominate in the equilibria. A zero signifies that reduction *failed* to take place. With the more stable carbonium ions, tests were also run in sulfuric acids more dilute than 75%. Reduction was never observed. [b] The reduction was measurably slow. [c] The cation is assumed to be in equilibrium with olefin.

HI Reductions.—The reductions by HI were more difficult to study because of the direct oxidation of HI to I_2 by sulfuric acid. I_2 formed even in phosphoric acid solutions, perhaps due to air oxidation. The experiments were limited to showing that $(C_6H_5)_3C^+$ and $(\text{mesityl})_2CH^+$ were rapidly reduced in 60% H_2SO_4 and that the 4-methoxytriphenylmethyl cation is inert to HI in 60% acid. In the latter case it was necessary to recover quantitatively the 4-methoxytriphenylmethanol since slow production of I_2 interfered with spectrophotometric determination of the cation. Recovery experiments were also performed on the reduction of the triphenylmethyl cation with the result that triphenylmethane was quantitatively isolated.

The limit for HI reductions are thus cations of pK_R^+ equal to about −5. This conclusion is in accord with examples of HI reductions reported in preparative organic chemistry.[10] Arylolefins,[11] arylalkanols,[12] aryl ketones,[13] highly conjugated olefins[14] and tetraphenylallene[15] are reduced. It is evident that these reactants form carbonium ions that are unstable enough to react and yet are not so unstable that significant concentrations of carbonium ions cannot be produced.

The reduction of 1,2-glycols by HI is general and gives yields of over 90% of the secondary iodoalkanes. Hexoses are reduced to 2- and 3-iodohexane,[10,16] glycerol and propylene glycol are reduced to 2-iodopropane,[17] erythritol to 2-iodobutane,[18] and ethylene glycol to ethylene.[19] This reduction of 1,2-glycols by HI is of particular interest because simple alkanols, including tertiary alcohols, are not reduced.[20] Ketones are also not reduced[21] which excludes a mechanism involving a pinacol rearrangement followed by reduction of the ketone.

A possible mechanism is replacement of hydroxyl by iodo, formation of the cyclic iodonium ion, and reaction of this ion with HI. This path could be brought into accord with exclusive abstraction of hydride by the primary carbon. An alternative mechanism featuring neighboring group participation in the glycol by adjacent -OH seems less likely in view of the absence of literature reports regarding hydride transfer reactions by glycols in strong mineral acid solutions.

The above discussion and conclusions are not applicable to those reductions by iodide ion which take place in neutral solution and do not appear to be catalyzed by acid. These neutral reductions are of two types, reduction of 1,2-dibromides[22]

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[10] In developing analytical procedures based on HI reductions, K. Miescher and J. R. Billeter (*Hev. Chim. Acta*, **22**, 601 (1939)) and H. K. Mitchell and R. J. Williams (*J. Am. Chem. Soc.*, **60**, 2723 (1938)) give summaries of the functional groups that are reduced by HI.

[11] S. Gabriel and J. Zimmermann, *Ber.*, **13**, 1680 (1880).

[12] C. S. Marvel, F. D. Hager and E. C. Caudle, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 219; D. A. Ballard and W. M. Dehn, *J. Am. Chem. Soc.*, **54**, 3970 (1932); A. Burawoy and J. T. Chamberlain, *J. Chem. Soc.*, 626 (1949); F. R. Japp and F. Klingman, *ibid.*, 770 (1893); A. E. Tschitschibabin, *Ber.*, **44**, 442 (1911); R. S. Morrell and S. O. Philips, *J. Soc. Chem. Ind.*, **59**, 144 (1940).

[13] S. Dev, *J. Indian Chem. Soc.* **25**, 323 (1948); A. Graebe, *Ber.*, **7**, 1626 (1874); H. Zook, unpublished work at Penna. State Univ.

[14] A. Polgar and L. Zechmeister, *J. Am. Chem. Soc.*, **65**, 1528 (1943).

[15] D. Vorlander and P. Winstein, *Ber.*, **56**, 1122 (1923).

[16] A. Michael and R. H. Hartman, *ibid.*, **40**, 140 (1907). This reference summarizes and corrects the extensive earlier work.

[17] M. Wurtz, *Ann. chim.*, [3] **63**, 125 (1861); H. Malbot, *ibid.*, [6] **19**, 347 (1890); E. Erlenmeyer, *Ann.*, **139**, 223 (1866).

[18] M. V. de Luynes, *Ann. chim.*, [2] **2**, 3 (1864).

[19] V. V. Korshek and S. A. Pavlova, *Izvest. Akad. Nauk S.S.S.R.*, 276 (1950).

[20] H. Stone and H. Schechter, *J. Org. Chem.*, **15**, 491 (1950).

[21] We have found that under conditions in which glycerol forms 2-iodopropane in 90% yield (ref. 17), acetone fails to yield any 2-iodopropane.

[22] For a review, see E. S. Gould, "Mechanism and Structure in

and reduction of α-iodo ketones, α-iodomalonic esters and related compounds.[23]

Reductions with $PtHCl[P(C_2H_5)_3]_2$ (I) and $IrH_2Cl[P(C_2H_5)_2(C_6H_5)]_3$ (II).[24]—The cations used were diphenylmethyl (A), 4-methyldiphenylmethyl (B), 4,4′-dimethyldiphenylmethyl (C), triphenylmethyl (D) and 4,4′-dimethoxydiphenylmethyl (E). The respective pK_R^+ values are −13.3, −11.6, −10.4, −6.63 and −5.71. The tests were conducted by adding 10 mg. of I or II to 5 ml. of a 10^{-5} molar solution of the cation.

Hydride I immediately reduced A, required a minute to reduce B, required five minutes to reduce C and required thirty minutes to reduce E. The more highly hindered D required several days for reduction. All tests were at 25°; A-C were in 82% H_2SO_4 and D and E were in 62% acid. The limiting value for reduction is about −5 for pK_R^+. The slowness of the reactions near the limiting pK_R^+ value inhibited a more precise evaluation. A further limitation was the lack of diarylmethyl cations with pK_R^+ around −5. The much more stable xanthyl cation (pK_R^+ −0.84) was not reduced as expected.

Hydride II decomposed slowly in 82% H_2SO_4 producing an orange gum and a brown solution. Despite this complication, the reduction of A in thirty minutes could be clearly observed; B-E were either very slow or failed to reduce.

In 96% H_2SO_4, I and II immediately evolved hydrogen and this reaction took precedence over the reduction of A.

Experimental

In the HBr reductions, the decolorization of the carbonium ions were so dramatic that simple visual observations were sufficient to detect quantitative reduction. Addition of 10 mg. of finely powdered NaBr to 10 ml. of 10^{-4} molar solutions of the carbonium ions caused complete decolorization in the cases indicated in Table I. Although Br_2 is produced in this reaction, its extinction coefficients in the visible region are insignificant relative to carbonium ions. However, if large amounts of NaBr are added, Br_2 is produced in large enough amounts by direct sulfuric acid oxidation to obscure the disappearance of the carbonium ions.

Even with the HI reductions, it is possible to observe virtually complete decolorization after several seconds if the amount of added KI is kept small, is finely ground, and is added with vigorous shaking.

The formation of carbonium ions by Br_2 oxidation was determined completely by spectrophotometric measurements using a Beckman DU spectrophotometer. The absorption spectra of Br_2 and the carbonium ions were sufficiently distinct in the four cases studied.

The products recovered from HBr and HI reductions were identified by comparison of m.p. and infrared spectra with authentic samples.

Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, p. 494.

(23) R. W. West, *J. Chem. Soc.*, **119**, 359 (1921); **121**, 2196 (1922); **125**, 710 (1924); **127**, 748 (1925); J. V. Baches, R. W. West and M. A. Whitely, *ibid.*, **119**, 360, 378 (1921); K. Meyer, *Ann.*, **380**, 212 (1911); M. Ehrenstein and M. Dunnenberger, *J. Org. Chem.*, **21**, 774 (1956); K. Balnović and V. Thaller, *ibid.*, **21**, 127 (1956); R. B. Wagner and J. M. Tome, *J. Am. Chem. Soc.*, **72**, 3477 (1950); M. L. Wolfrom and R. L. Brown, *ibid.*, **65**, 1516 (1943).

(24) We are indebted to Dr. Bernard L. Shaw of the University of Leeds for samples of these two transition metal hydrides and to Dr. Joseph Chatt of Imperial Chemical Industries Ltd. for discussions of these possibilities.

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The Carbonylation of Organoboranes. I. The Carbonylation of Trialkylboranes. A Novel Synthesis of Trialkylcarbinols[1]

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Reactions of carbon monoxide with trialkylboranes have been discovered which gave a variety of novel products, depending on reaction temperature and solvent. Hexaalkyl-2,5-diboradioxanes and trialkylcarbinylboronic acids or anhydrides were obtained in near-quantitative yields. A reaction mechanism involving three boron-to-carbon alkyl migrations is proposed. Oxidation or hydrolysis of the intermediates gave the corresponding di- and trialkylcarbinols and dialkyl ketones in near theoretical yields.

Introduction

Although extensive research has lately been directed at the preparation of organoboranes,[3] very little has been reported on attempts to uncover new reactions of organoboranes.[4] Such studies seemed desirable in view of the extreme reactivity of organoboranes toward molecular oxygen. Although attempts to use organoboranes as "Grignard-type reagents" by reaction with carbon dioxide were unsuccessful, carbon monoxide reacted exothermally with trialkylboranes to give products in which novel rearrangements of the alkyl groups from boron to carbon had occurred.

Results and Discussion

When trialkylboranes (I) were carbonylated in ethers, hydrocarbons or in the absence of solvent, a mixture of products was obtained. When water or another hydroxylic solvent was used as the reaction medium, single products were obtained. Carbonylation of trialkylboranes at temperatures between 25° and 75° in the presence of excess water gave excellent yields of 2,3,3,5,6,6-hexaalkyl-2,5-dibora-1,4-dioxanes (II); whereas

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[1] Presented at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1962; Abstracts of Papers, p. 9-Q.

[2] Exploratory Chemicals Section, California Research Corporation, Richmond, Calif.

[3] Some examples are: H. C. Brown, *Tetrahedron*, **12**, 117 (1961); H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 2544 (1961); M. F. Hawthorne, *ibid.*, **83**, 2541 (1961); and E. L. Muetterties, *ibid.*, **82**, 4163 (1960).

[4] Recent review articles are: H. C. Brown, in "Organometallic Chemistry, ed. H. Zeiss, Reinhold Publishing Corp., New York, N. Y., 1960, pp. 150–193; H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962; W. Gerrard, "The Organic Chemistry of Boron, Academic Press, Inc., New York, N. Y., 1961.