

$\delta$  3.6 (m, 1 H), 2.2-1.6 (m, 3 H), 1.4-1.1 (m, 5 H), 1.0 (s, 9 H), 0.9 (m, 1 H), 0.4-0.1 (m, 3 H); IR 3350, 2950, 1369, 1210, 1070  $\text{cm}^{-1}$ . In addition, 14 (7 mg, 8%) was obtained.

**4-tert-Butyl-1-hydroperoxy-9-oxabicyclo[4.2.1]nonanes (16 and 17).** A solution of 14 (92 mg, 0.50 mmol) was rearranged in THF (2 mL) and 90%  $\text{H}_2\text{O}_2$  (2 mL, 72 mmol  $\text{H}_2\text{O}_2$ ) containing  $\text{TsOH}\cdot\text{H}_2\text{O}$  (120 mg, 0.60 mmol) for 48 h according to procedure F. Preparative TLC of the crude product (50 mg) yielded an inseparable mixture of 16 and 17 (31 mg, 33%) as a 1:1 mixture by  $^1\text{H}$  NMR as shown by integration of the carbonyl signals at  $\delta$  4.17 (16) and 4.70 (17).

**4-tert-Butyl-1-hydroperoxy-9-oxabicyclo[4.2.1]nonane (17).** A solution of 15 (44 mg, 0.24 mmol) was rearranged in THF (1 mL) and 90%  $\text{H}_2\text{O}_2$  (1 mL, 36 mmol  $\text{H}_2\text{O}_2$ ) containing  $\text{TsOH}\cdot\text{H}_2\text{O}$  (24 mg, 0.12 mmol) for 20 min according to procedure F. Preparative TLC of the crude product (64 mg) yielded 17 (43 mg, 84%): mp 94-95  $^\circ\text{C}$ ;  $^1\text{H}$  NMR  $\delta$  8.7 (s, 1 H), 4.70 (m, 1 H), 2.5 (m, 1 H), 2.3-1.2 (m, 10 H), 0.90 (s, 9 H); IR 3300 (br), 2960, 1460, 1360, 1195, 1045, 1000  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{12}\text{H}_{22}\text{O}_3$ : C, 67.25, H, 10.35. Found: C, 67.26; H, 10.38.

**2-(1-Cycloheptenyl)ethyl brosylate (12):** mp 31-32  $^\circ\text{C}$ .  $^1\text{H}$  NMR  $\delta$  7.7 (4 H), 5.6 (t, 1 H,  $J = 8.1$  Hz), 4.1 (t, 2 H,  $J = 7.8$  Hz), 2.3 (t, 2 H,  $J = 7.5$  Hz), 2.0 (br m, 4 H), 1.8-1.2 (m, 6 H);  $^{13}\text{C}$  NMR  $\delta$  138.44, 132.48, 129.91, 129.32, 128.72, 128.36, 69.61, 39.39, 32.60, 32.24, 28.31, 26.88, 26.52; IR 2920, 2860, 1570, 1360, 1180, 960, 876  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{15}\text{H}_{20}\text{BrO}_3\text{S}$ : C, 50.15, H, 5.33. Found: C, 50.25, H, 5.21.

**1-Hydroperoxy-10-oxabicyclo[5.2.1]decane (7):** mp 62-63  $^\circ\text{C}$ ;  $^1\text{H}$  NMR  $\delta$  8.3 (s, 1 H), 4.7 (s, 1 H), 2.4-1.2 (br m, 14 H);  $^{13}\text{C}$  NMR  $\delta$  116.09, 80.63, 36.53, 34.63, 31.23, 28.79, 27.30, 27.18, 24.38; IR 3331, 2923, 2851, 1469, 1327, 1161, 1044, 963  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_9\text{H}_{16}\text{O}_3$ : C, 62.77; H, 9.36. Found: C, 62.69; H, 9.15. **Phenylurethane of 1-hydroxy-10-oxabicyclo[5.2.1]decane:** mp 83-84.5  $^\circ\text{C}$ ,  $^1\text{H}$  NMR  $\delta$  7.3 (m, 5 H), 6.7 (br m, 1 H), 4.9 (m, 1 H), 2.7-2.4 (m, 4 H), 2.3-2.0 (m, 2 H), 1.9-1.4 (br m, 8 H); IR 3320, 2940, 2860, 1750, 1710, 15808, 1549, 1430, 1210, 1170  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{16}\text{H}_{21}\text{NO}_3$ : C, 69.79; H, 7.69. Found: C, 69.72; H, 7.74.

**2-(1-Cyclooctenyl)ethyl brosylate<sup>11</sup> (3):**  $^1\text{H}$  NMR  $\delta$  7.7 (m, 4 H), 5.3 (t, 1 H,  $J = 8.0$  Hz), 4.1 (t, 2 H,  $J = 7.1$  Hz), 2.4 (t, 2 H,  $J = 7.1$  Hz), 2.1-1.9 (br m, 4 H), 1.4 (br m, 8 H);  $^{13}\text{C}$  NMR  $\delta$  134.85, 132.71, 132.47, 129.31, 129.13, 127.70, 69.66, 36.70, 29.61, 28.78, 28.54, 27.31, 26.33, 26.10; IR 2924, 2854, 1577, 1363, 1186, 1096, 1069, 951, 914, 624, 781  $\text{cm}^{-1}$ .

(11) Paquette, L. A.; Hensel, K. A.; *J. Am. Chem. Soc.* **1975**, *97*, 4649-4658.

**1-Hydroperoxy-11-oxabicyclo[6.2.1]undecane (8):**  $^1\text{H}$  NMR  $\delta$  9.3 (s, 1 H), 4.6 (br m, 1 H), 2.4-2.1 (m, 2 H), 1.9-1.1 (m, 14 H);  $^{13}\text{C}$  NMR  $\delta$  116.14, 81.52, 24.57, 33.38, 31.95, 29.50, 29.32, 26.94, 22.29, 21.87; IR 3330 (br), 2930, 2860, 1462, 1439, 1333, 1312, 1135, 1064, 1042, 978  $\text{cm}^{-1}$ .

**2-(1-Cyclododecyl)ethyl brosylate (4):** mp 39.5-41.5  $^\circ\text{C}$ ;  $^1\text{H}$  NMR  $\delta$  7.7 (m, 4 H), 5.1 (t, 1 H,  $J = 7.0$  Hz), 4.1 (t, 2 H,  $J = 7.2$  Hz), 2.4-1.8 (br m, 6 H), 1.8-1.2 (br m, 12 H); IR 2940, 2860, 1580, 1470, 1360, 1180, 960, 900, 830, 780  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{18}\text{H}_{26}\text{BrO}_3\text{S}$ : C, 53.87; H, 6.28. Found: C, 53.78; H, 6.53.

**1-Hydroperoxy-13-oxabicyclo[8.2.1]tridecane (9):**  $^1\text{H}$  NMR  $\delta$  8.3 (br, 1 H), 4.4 (m, 1 H), 1.9-1.1 (large m, 24 H); IR 3330, 2930, 2862, 1463, 1430, 1330, 1140, 1055, 1045  $\text{cm}^{-1}$ . **Phenylurethane of 13-oxabicyclo[8.2.1]tridecan-1-ol:** mp 109.5-110  $^\circ\text{C}$ ;  $^1\text{H}$  NMR  $\delta$  7.3 (m, 5 H), 6.6 (br m, 1 H), 5.1 (br m, 1 H), 1.8-1.2 (br m, 20 H); IR 3450, 2940, 2860, 1730, 1540, 1450, 1220, 1090  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{19}\text{H}_{27}\text{NO}_3$ : C, 71.89; H, 8.57. Found: C, 72.06; H, 8.63.

**2-(1-Cyclododecyl)ethyl brosylate (5):** mp 29-30.5  $^\circ\text{C}$  (only the trans product was solid);  $^1\text{H}$  NMR  $\delta$  7.7 (m, 4 H), 5.3 (t, 1 H,  $J = 7.2$  Hz), 4.0 (t, 2 H,  $J = 7.0$  Hz), 2.4 (t, 2 H,  $J = 7.0$  Hz), 2.2-1.7 (br m, 4 H), 1.6-1.1 (br m, 16 H); IR 2920, 2850, 1570, 1470, 1380, 1190, 1070, 1010, 820  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{20}\text{H}_{30}\text{BrO}_3\text{S}$ : C, 55.94; H, 6.81. Found: C, 55.83; H, 6.92.

**1-Hydroperoxy-15-oxabicyclo[10.2.1]pentadecane (10):**  $^1\text{H}$  NMR  $\delta$  8.3 (br, 1 H), 4.4 (br m, 1 H), 2.0-1.0 (br, 24 H); IR 3334, 2936, 2856, 1463, 1429, 1333, 1313, 1137, 1064, 1042, 975  $\text{cm}^{-1}$ . **Phenylurethane of 15-oxabicyclo[10.2.1]pentadecan-1-ol:** mp 132-133  $^\circ\text{C}$ ;  $^1\text{H}$  NMR  $\delta$  7.93 (m, 5 H), 6.5 (m, 1 H), 4.7 (m, 1 H), 2.1-1.1 (br m, 24 H); IR 3330, 2940, 2860, 1740, 1710, 1600, 1540, 1440, 1220  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{21}\text{H}_{31}\text{NO}_3$ : C, 73.01; H, 9.04. Found: C, 73.11; H, 9.09.

**Acknowledgment.** This work was supported by the National Institute of Health Grant GM33034. We thank Boeing Co., for the gift of the Nicolet Technology Inc. 200-MHz NMR spectrometer. T.S.L. thanks the graduate school of Washington State University for an assistantship.

**Registry No.** 1, 83321-29-3; 1 (alcohol), 3197-68-0; 2, 86669-50-3; 3, 41299-58-5; 3 (methyl acetate deriv), 76519-82-9; 3 (alcohol), 21336-24-3; 4, 86669-52-5; 5, 86669-54-7; 6, 86669-49-0; 7, 86669-51-4; 7 (phenylurethane), 99035-15-1; 8, 86669-47-8; 9, 86669-53-6; 9 (phenylurethane), 99035-16-2; 10, 86669-55-8; 10 (phenylurethane), 99035-17-3; 11, 3301-81-3; 12, 21336-30-1; 13, 21336-25-4; 14, 20702-59-4; 15, 20707-15-7; 16, 99035-12-8; 17, 99095-80-4; 18, 99035-13-9; 19, 99035-14-0; 20, 20647-96-5;  $\text{B}_2\text{Cl}_4$ , 98-58-8;  $(\text{H}_3\text{CO})_2\text{POCH}_2\text{CO}_2\text{CH}_3$ , 5927-18-4; cyclooctanone, 502-49-8; methyl cyclooctylideneacetate, 99035-18-4.

## Hydroxide Ion Initiated Reactions under Phase Transfer Catalysis Conditions. 9. Dehydrohalogenation of (Haloethyl)benzenes by Quaternary Ammonium Salts<sup>1</sup>

Marc Halpern, Hayder A. Zahalka, Yoel Sasson,\* and Mordecai Rabinovitz\*

Department of Organic Chemistry, The Institute of Chemistry and Casali Institute of Applied Chemistry,  
School of Applied Science & Technology, The Hebrew University of Jerusalem, 91904 Jerusalem, Israel

Received May 28, 1985

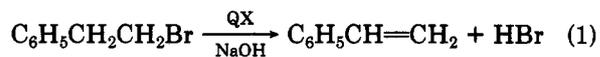
Elimination of HCl and HBr from (1- and (2-haloethyl)benzenes in the presence of aqueous sodium hydroxide and quaternary ammonium salts which cannot extract hydroxide anion to the organic phase is shown to proceed via a reverse phase transfer process. The catalyst QX promotes the elimination and forms QX-HX adduct which is neutralized at the interphase by the hydroxide base. First-order kinetics is observed under conditions in which the catalyst is stable. Complicated kinetics is obtained when decomposition of the catalyst takes place simultaneously with the reaction.

The two-phase dehydrogenation of alkyl halides in the presence of alkali hydroxide and quaternary onium salts

(quats, QX) phase transfer catalysts have found numerous preparative applications in the synthesis of olefins and

acetylenes as was reviewed by Starks<sup>2</sup> and by Dehmlow.<sup>3</sup>

A well-known example is the dehydrobromination of (2-bromoethyl)benzene to yield styrene<sup>4</sup> (eq 1).



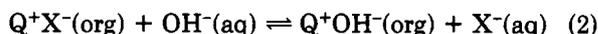
This reaction takes place at 70 °C in presence of 50% aqueous sodium hydroxide solution and practically any quaternary ammonium salt that has some solubility in the organic phase.

Less active halides react only in the presence of specific quats which sometimes are used in stoichiometric excess. The dehydrobromination of dibromostilbene to diphenylacetylene,<sup>5</sup> for example, required the presence of 3 equiv of tetra-*n*-butylammonium hydrogen sulfate (NBu<sub>4</sub>·HSO<sub>4</sub>) in order to obtain quantitative yields. Other NBu<sub>4</sub> salts, e.g., the bromide or the iodide, were found to be inactive in this reaction.

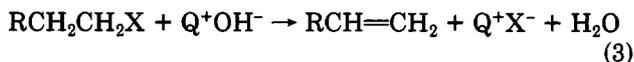
Interestingly, while the presence of a quat is essential for this type of dehydrohalogenation, the alkaline base can be avoided if higher temperature is applied. Gaseous HCl or HBr is released in this case.<sup>6,7</sup>

Two different mechanisms were proposed in the literature for these eliminations:<sup>3</sup>

(a) **Extraction Mechanism.** Hydroxide ion is extracted into the organic phase via interfacial anion exchange (eq 2). The quat hydroxide is the active base



which induces the elimination in the organic phase (eq 3).

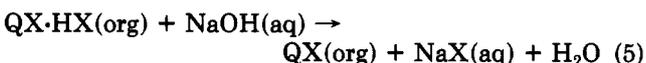


The ion pair Q<sup>+</sup>OH<sup>-</sup> is recycled for another catalytic cycle.

(b) **Reverse Transfer Mechanism.** In this mechanism, proposed by Dehmlow,<sup>3</sup> the organic phase base is the QX itself which reacts with the substrate to yield the product olefin and the adduct QX·HX (eq 4). The adduct



QX·HX, which is stabilized by intramolecular hydrogen bonding<sup>8</sup> is neutralized at the interphase to recycle QX (eq 5).



It was shown by several authors<sup>9-12</sup> that the extraction of hydroxide anion by liquid anion exchangers (eq 1) can be observed only in systems where highly lipophilic am-

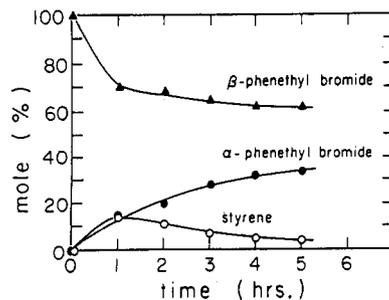


Figure 1. Elimination and isomerization of (2-bromoethyl)benzene in presence of 5 mol % NBu<sub>4</sub>Br at 155 °C.

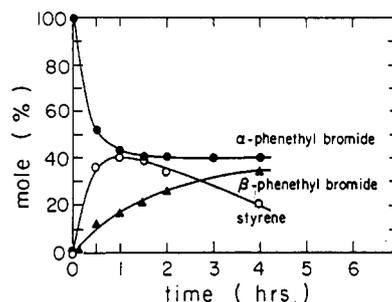


Figure 2. Elimination and isomerization of (1-bromoethyl)benzene in presence of 5 mol % NBu<sub>4</sub>Br at 155 °C.

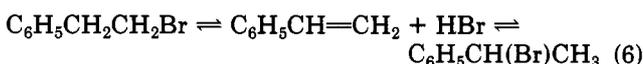
monium cation paired with hydrophilic anion (e.g., hydrogen sulfate) is contacted with very concentrated or, preferably, solid caustic base. Mechanism a can therefore be expected to operate only under these specific conditions.

In a previous article in this series we reported<sup>13</sup> the mechanism of the elimination reaction 1 in presence of tetra-*n*-octylammonium bromide (NOct<sub>4</sub>Br). It was shown that with this catalyst a zero-order kinetics is observed with activation energy of 8 kcal/mol. We claimed that the mechanism is via hydroxide ion extraction and that the quat hydroxide ion pair (QOH) is so reactive in promoting the elimination step (eq 3) that the extraction process (eq 2) becomes rate controlling.

In this work we studied the behavior of the phase transfer catalyzed dehydrohalogenation of phenyl ethyl halides under conditions where hydroxide ion extraction is negligible and the main mechanism is of type b.

## Results and Discussion

We have initially examined the interaction of (2-bromoethyl)benzene (1) with quaternary ammonium salts. A 5 mol % solution of NBu<sub>4</sub>Br in 1 was heated in a thermostatic bath while samples were taken and analyzed by gas chromatography. At 100 °C a stoichiometric elimination reaction took place, yielding 5 mol % of styrene. The mixture was then heated to 140 °C where some HBr gas started to evolve. To our surprise the solution contained in addition to the elimination product styrene the isomerization product (1-bromoethyl)benzene (2). Following the composition change of the same mixture at 155 °C has revealed that the behavior is of a reversible consecutive reaction with styrene as an intermediate (eq 6). The composition-time profile is shown in Figure 1.



(1) Part 8: Halpern, M.; Cohen, Y.; Sasson, Y.; Rabinovitz, M. *Nouv. J. Chim.* 1984, 8, 443.

(2) Starks, C. M.; Liotta, C. "Phase Transfer Catalysis Principles and Techniques"; Academic Press: New York, 1978; pp 330-337.

(3) Dehmlow, E. V.; Dehmlow, S. S. "Phase Transfer Catalysis", 2nd ed.; Verlag Chemie: Weinheim, 1983; pp 177-182.

(4) Dockx, J. *Synthesis* 1973, 441.

(5) Gorgoes, A.; Le Coq, A. *Tetrahedron Lett.* 1976, 4521.

(6) Sennewald, K.; Gehrmann, K.; Viertel, G. German Patent 1 271 107, 1968.

(7) Lutz, E. F.; Kelly, J. T.; Hall, D. W. British Patent 1 112 068, 1968.

(8) Zahalka, H. A.; Sasson, Y. *J. Chem. Soc., Chem. Commun.* 1984, 1581 and references therein.

(9) Dehmlow, E. V.; Lissel, M. *Tetrahedron* 1981, 37, 1653.

(10) Landini, D.; Maia, A. *J. Chem. Soc., Chem. Commun.* 1984, 1041.

(11) Dehmlow, E. V.; Slopianka, M.; Heider, J. *Tetrahedron Lett.* 1977, 2361.

(12) Dehmlow, E. V.; Thieser, R.; Sasson, Y.; Pross, E. *Tetrahedron* 1985, 41, 2972.

(13) Halpern, M.; Sasson, Y.; Rabinovitz, M. *J. Org. Chem.* 1984, 49, 2011.

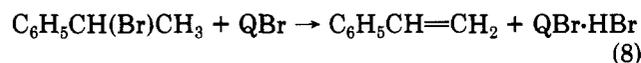
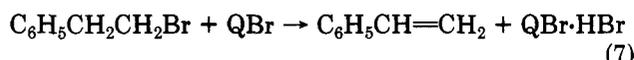
(14) Parker, A. J.; Ruane, M.; Biale, G.; Winstein, S. *Tetrahedron Lett.* 1968, 2113.

**Table I. Elimination of Hydrogen Halide from Substituted (1-Haloethyl)benzenes with NBu<sub>4</sub> Catalysts in the Presence of 50% Sodium Hydroxide Solution at 75 °C (Eq 8)**

expt	X	Y	Z <sup>-</sup>	conversion, %		rate constant 10 <sup>2</sup> k, min <sup>-1</sup>
				60 min	120 min	
1	Cl	H	HSO <sub>4</sub>	65	85 <sup>c</sup>	1.3
2	Cl	Cl	HSO <sub>4</sub>	58	83	1.3
3	Cl	Br	HSO <sub>4</sub>	60	82	1.3
4	Cl	CH <sub>3</sub>	HSO <sub>4</sub>	60	86	1.3
5	Br	CH <sub>3</sub>	HSO <sub>4</sub>	46	68	0.97
6	Cl	CH <sub>3</sub>	Br	44	65	0.94
7	Cl	CH <sub>3</sub>	I	21	40	0.4
8 <sup>d</sup>	Cl	H	HSO <sub>4</sub>	50	53	
9 <sup>d,e</sup>	Cl	H	Cl	60	61	

<sup>a</sup>For experimental conditions and analysis, see Experimental Section. <sup>b</sup>Determined by <sup>1</sup>H NMR. <sup>c</sup>93% after 180 min. <sup>d</sup>At 90 °C. <sup>e</sup>With aliquot 336 catalyst.

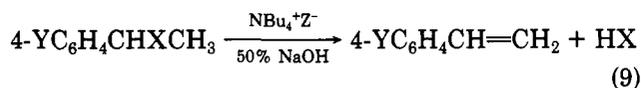
The reverse reaction, starting with 2 and NBu<sub>4</sub>Br, behaved similarly, but the initial rate was found to be four times higher and the maximum concentration of the intermediate styrene was accordingly higher. The profile of the reverse reaction is shown in Figure 2. It is apparent that NBu<sub>4</sub>Br functions as a base in these systems and, at the first stage, absorbs 1 equiv of HBr from each substrate (eq 7 and 8).



When a temperature higher than 140 °C is applied the adduct decomposes to release HBr, which consequently adds to styrene via both Markovnikov and anti-Markovnikov addition. The overall reaction is according to eq 6.

Upon removal of the hydrobromic acid from the system, e.g., by the presence of a base, the isomerization is avoided, and a clean elimination is obtained even at 75 °C.

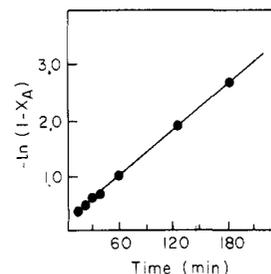
A series of substituted (1-haloethyl)benzenes was thus reacted with an excess of 50% (w/w) aqueous sodium hydroxide solution in presence of 5 mol % of various NBu<sub>4</sub> catalysts at 75 °C with efficient stirring (eq 9). The



reactions 8 were followed by <sup>1</sup>H NMR spectra of organic phase samples taken from the reaction mixtures and by halide titration in the aqueous phase. Table I presents the conversions after 60 and 120 min and the first-order rate constants of several runs. A procedure for synthesis of 4-bromostyrene according to eq 8 with continuous removal of the product by distillation under vacuum is given in the Experimental Section. Figure 3 presents a kinetic profile of reaction 9 presented as a first-order reaction after 15 min of reaction where X = H, Y = Cl, and Z = HSO<sub>4</sub> under the condition of Table I. The first-order behavior is expected with the large excess of sodium hydroxide used and with a constant catalyst concentration.

Analysis of the reaction profile indicate that initially a rapid rate is observed up to conversion of 15% followed by a first-order kinetics which is valid up to conversion of 93% where the reaction slows down. The initial rapid rate is not observed when bromide catalyst is used.

The data in Table I clearly indicate that the rate of the elimination process is practically independent of the substituent Y, suggesting that no ionic intermediate is involved in the elimination mechanism.<sup>15,16</sup>



**Figure 3.** First-order kinetics of the elimination of (1-chloroethyl)benzene in presence of NBu<sub>4</sub>-HSO<sub>4</sub>. Reaction conditions: 70.9 mmol of substrate, 35 mL of 50% NaOH solution, 3.55 mmol of TBA-HSO<sub>4</sub>; 75 °C; stirring at 1000 rpm.

The main effect on the rate can be attributed to the nature of the anion paired with the quaternary ammonium cation in the organic phase. Three different anions are present in the aqueous phase of a typical reaction 9 when the process is in progress: hydroxide, the anion originally introduced with the catalyst, and the halide released by elimination. The anion, which will be preferentially extracted as an ion pair and eventually will determine the nature of the actual catalyst, depends on the aqueous-phase concentration of the anions and their extraction selectivity coefficient.<sup>17,18</sup> Based on the literature data it can be concluded that iodide or bromide, even if they originate only by the catalyst (and are thus limited to catalytic quantities), will still be the major anion in the organic phase and will then determine the rate of elimination.<sup>19</sup>

In systems where only hydrogen sulfate (or sulfate) anions are present besides the hydroxide one should expect to observe actual extraction of hydroxide anion<sup>10</sup> to the organic phase until some halide is released to the mixture by elimination and occupies the catalyst.

Based on our results it can be safely argued that the catalytic activity decreases in the order QCl > QBr > QI, which is in accordance with decreasing basicity and decreasing nucleophilicity in the aprotic apolar medium.<sup>20</sup> The ion pair QOH is significantly more active than the

(16) Additional evidence that a nonionic intermediate is involved in this mechanism can be found in the fact that when meso-1,2-dibromo-1,2-diphenylethane is eliminated under the conditions reported in ref 5 but in presence of 100 mol % of NBu<sub>4</sub>HSO<sub>4</sub> cis-bromostilbene was formed exclusively. The *d,l* isomer afforded *trans*-bromostilbene selectively. <sup>1</sup>H NMR data: [*cis*-bromostilbene] 7.259–7.362 (5 H), 7.159 (s, 1 H), 7.092–7.114 (3 H), 6.927–6.959 (2 H), [*trans*-bromostilbene] 7.642–7.720 (4 H), 7.518–7.555 (1 H), 7.331–7.424 (5 H) 7.214 (s, 1 H) ppm.

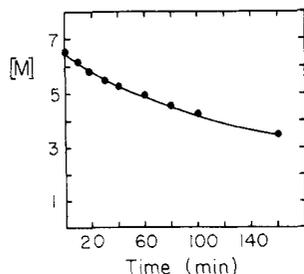
(17) Gordon, J. E.; Kutina, R. E. *J. Am. Chem. Soc.* 1977, 99, 3903.

(18) Bar, R.; Bar, L. K.; Sasson, Y.; Blum, J. *Anal. Chim. Acta* 1983, 154, 203.

(19) Bar, R.; de la Zerda, J.; Sasson, Y. *J. Chem. Soc., Perkin Trans. 2* 1984, 1875.

(20) Parker, A. J. *J. Chem. Soc.* 1961, 1328.

(15) Lloyd, D. J.; Parker, A. J. *Tetrahedron Lett.* 1970, 5029.



**Figure 4.** Reaction profile of the elimination of HBr from (2-bromoethyl)benzene with TEBA-Br catalyst. Reaction conditions: 66.5 mmol of substrate, 840 mg of toluene, 35 mL of 50% NaOH, 0.665 mmol of TEBA-Br; 75 °C; stirring at 1000 rpm.

corresponding halides, but its presence is limited to the very initial stages of reactions where hydrogen sulfate catalyst is used. It is probably responsible for the initial rapid rate observed when using hydrogen sulfate catalyst.

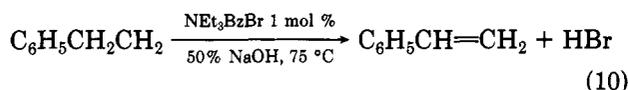
We cannot comment at this stage on the activity of QHSO<sub>4</sub> or Q<sub>2</sub>SO<sub>4</sub>, which are present, though in minor amounts in some of the systems.

The effect of certain anions on the behavior of base-promoted PTC elimination reactions was reported. Both nitrate<sup>21</sup> and *tert*-butoxide<sup>22</sup> anions had cocatalytic effect on eliminations of brominated (2-bromoethyl)benzenes to yield bromostyrenes. Since these anions have relatively high extraction coefficients we can assume that Q<sup>+</sup>NO<sub>2</sub><sup>-</sup> and Q<sup>+</sup>(*O-t*-Bu)<sup>-</sup> are active elimination catalysts.

Since in these processes the composition of the quaternary catalyst in the organic phase is changing with the progress of the reaction, the observed kinetics in certain cases is quite complicated.<sup>17</sup> The measured catalytic activity is the combination of activities of the various species of the quat at a given time.

Another factor that should be taken into consideration is the deactivation of the catalyst via thermal decomposition and via the Hofmann elimination<sup>10</sup> which is quite pronounced under our strong alkaline conditions. Figure 3 shows that at 75 °C after 93% conversion the reaction practically stops. At 90 °C the reaction stopped after 53% conversion. This can be attributed to the decomposition of the catalyst. We have verified that addition of fresh amount of catalyst resumes the reaction and also that the decomposition product, namely, tri-*n*-butylamine, is not catalytically active in the elimination process.<sup>23</sup>

A clear catalyst deactivation phenomenon was observed when the more sensitive triethylbenzylammonium (NEt<sub>3</sub>Bz) catalyst is used. We have applied triethylbenzylammonium bromide (NEt<sub>3</sub>BzBr) (1 mol %) with large excess of 50% aqueous sodium hydroxide solution for the elimination of 1 (eq 10).



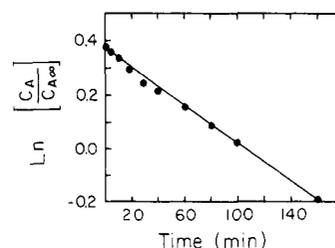
A typical reaction profile is shown in Figure 4. This profile does not fit a simple first- or second-order kinetics and is completely different from the zero-order profile obtained for the same reaction when catalyzed by NOct<sub>4</sub>Br.<sup>13</sup> The apparent activation energy measured for reaction 10, 22 kcal/mol<sup>24</sup> is again in sharp difference from

(21) Daren, S. L. J.; Vofsi, D.; Asscher, M. U.S. Patent 4 292 453, 1981.

(22) Jackisch, P. F. U.S. Patent 4 423 262, 1983.

(23) The observation that tertiary amines are not active in the elimination suggest that the reverse phase transfer process proposed by Starks (ref 2) is apparently not possible under these conditions.

(24) Based on initial rate measurements, at 65 °C (-0.020 mol L<sup>-1</sup> min<sup>-1</sup>), 75 °C (-0.037 mol L<sup>-1</sup> min<sup>-1</sup>), 85 °C (-0.132 mol L<sup>-1</sup> min<sup>-1</sup>).



**Figure 5.** Deactivation of the NEt<sub>3</sub>BzBr catalyst presented by plot of a  $\ln \ln (C_A/C_{A0})$  vs. time. Data from Figure 4.

the 8 kcal/mol measured for NOct<sub>4</sub>Br.

Since the extraction of hydroxide anion by the hydrophilic TEBA catalyst is highly improbable and the only other anion in the system is bromide we have reasons to believe that the active catalyst is TEBA-Br throughout the reaction. The fact that the reaction stops after 77.5% conversion indicates deactivation of the catalyst. Additional evidence can be found in the observation that addition of fresh catalyst resumed the elimination process. If we assume that at a constant catalyst concentration with the large excess of hydroxide base the elimination follows a pseudo-first-order kinetics the rate equation under these conditions is as in eq 11, where [s] is the concentration of

$$\text{rate} = -\frac{d[s]}{dt} = k[s] \quad (11)$$

the substrate 1 and  $k$  is the observed first-order rate constant. If the catalyst decomposes by a first-order reaction for which the decomposition rate constant is  $k_d$  it can be shown eq 12 obtains,<sup>25</sup> where [s]<sub>∞</sub> is the final con-

$$\ln \ln ([s]/[s]_\infty) = \ln (k/k_d) - k_d t \quad (12)$$

centration of the substrate. A plot of  $\ln \ln ([s]/[s]_\infty)$  as a function of time should yield a straight line with intercept  $= \ln (k/k_d) = \ln \ln ([s]_0/[s]_\infty)$  and slope  $= -k_d$ .

Figure 5 presents the data of Figure 4 plotted according to eq 12. A straight line is obtained from which we have calculated  $k = 76.57 \times 10^{-3} \text{ min}^{-1}$  and  $k_d = 3.574 \times 10^{-3} \text{ min}^{-1}$ .

The figure obtained for the rate of catalyst decomposition is 1 order of magnitude smaller than the figure measured by Landini<sup>10</sup> for decomposition of quat hydroxide at 25 °C. This is additional evidence that our catalyst is not in a hydroxide form during the reaction.

It can be concluded that the mechanism b presented in the introduction can explain the behavior of many PTC elimination reactions where the hydroxide anion extraction is not possible. In this mechanism the catalyst functions both as a base and as a HX carrier.

## Experimental Section

**Isomerization and Elimination of 1 and of 2.** In a 50-mL flask equipped with a magnetic stirrer and reflux condensed and heated by a thermostatic oil bath were mixed 5 g of 1 (or of 2) (27 mmol) and 0.435 g of TBAB (1.35 mmol) and 300 mg of 1-methylnaphthalene (internal standard) at 155 °C. Samples were analyzed by Hewlett-Packard 5790 gas chromatograph with 5% phenyl methyl silicone 25 m × 0.31 mm capillary column (N<sub>2</sub> carrier gas, flow rate 2 mL/min, FID detector; column temperature 80–250 °C at 10°/min). Retention times were as follows: styrene, 1.02 min; (1-bromoethyl)benzene, 4.83 min; (2-bromoethyl)benzene, 6.35 min; 1-methylnaphthalene, 9.19 min.

**Dehydrohalogenation of Substituted (1-Bromoethyl)benzene (Table I).** The reaction vessel consisted of a 50-mL flask equipped as in the previous experiment. 3 (70.9 mmol) was

(25) Levenspiel, O. "Chemical Reaction Engineering" Wiley: New York, 1972; Chapter 15.

stirred with 35.0 mL of 50% NaOH (660 mmol) in the presence of 1.21 g of  $\text{NBu}_4\text{HSO}_4$  (3.55 mmol) at 75 °C and 1000 rpm. In experiments 1-3 and 8, 1.19 g of durene (8.88 mmol) was also present as NMR internal standard. Samples were taken for NMR analysis at regular intervals. Conversions were determined by integration band area ratio between the methyl doublet (1.70 ppm,  $J = 6.5$  Hz) or the durene methyl singlet (2.09 ppm) and the ring methyl singlet (2.17 ppm). The styrene vinyl hydrogens (5.0-6.7 ppm) were used as a double check.

**Synthesis of 4-Bromostyrene.** 4-Bromo(1-chloroethyl)-benzene (11 g, 0.05 mol), 20 g of solid sodium hydroxide (0.5 mol), and 1.15 g of aliquat 336 (2.5 mmole) were placed in a 50-mL flask equipped with a magnetic stirrer and a distillation condenser under 1 mmHg of vacuum. The mixture was heated by an oil bath at 70 °C and the material distilled at 42-45 °C was collected. Product (6.3 g) was obtained, which by  $^1\text{H}$  NMR spectrum was found to contain 94% of 4-bromostyrene and 6% of the starting material (yield 64%).

$^1\text{H}$  NMR: [4-bromo(1-chloroethyl)benzene] 7.18 (AB,  $J = 8$  Hz, 4 H, Ar), 4.87 (qt,  $J = 6$  Hz, 1 H), 1.78 (db,  $J = 6$  Hz, 3 H), [4-bromostyrene] 7.12 (AB,  $J = 8$  Hz, 4 H, Ar), 6.20-6.66 (m, 1

H, vinylbenzyl), 5.35-5.63 (m, 1 H, vinyl cis to ring), 5.00-5.17 (m, 1 H, vinyl trans to ring) ppm.

**Dehydrobromination of (2-Bromoethyl)benzene.** The reaction vessel consisted of 100-mL three-necked round-bottomed flask equipped with an rpm-calibrated mechanical stirrer, a thermometer (immersed in the reaction mixture during agitation), and a sampling port. The reaction vessel was immersed in a stirred thermoregulated bath (contract thermometer  $\pm 0.5$  °C). A solution of 12.30 g of 1 (66.5 mmol) and 840 mg of toluene (9.12 mmol) as internal GC standard as mixed with 35.0 mL of 50% NaOH (660 mmol) for 15 min. GC analysis showed no conversion.  $\text{NEt}_3\text{BzBr}$  (181 mg, 0.665 mmol) was then added and the time taken, and samples taken at regular intervals were injected into a GC column: 15% DEGS on Chromosorb P, 2 m,  $1/84$  in. copper tube operating at 95 °C ( $\text{N}_2$  flow 1  $\text{cm}^3/\text{s}$ ). Conversions were determined by a calibration graph. Clear resolution of the peaks was obtained with retention times of 1.1 min (toluene), 1.5 min (styrene), and 4.9 min (1).

**Acknowledgment.** This research was partially supported by the Deutsche Forschungsgemeinschaft.

## The Synthesis and Ionization Constants of Some Derivatives of 1-Biphenylenol<sup>1</sup>

Jack Hine,\* Soonkap Hahn, David E. Miles, and Kyunghye Ahn

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

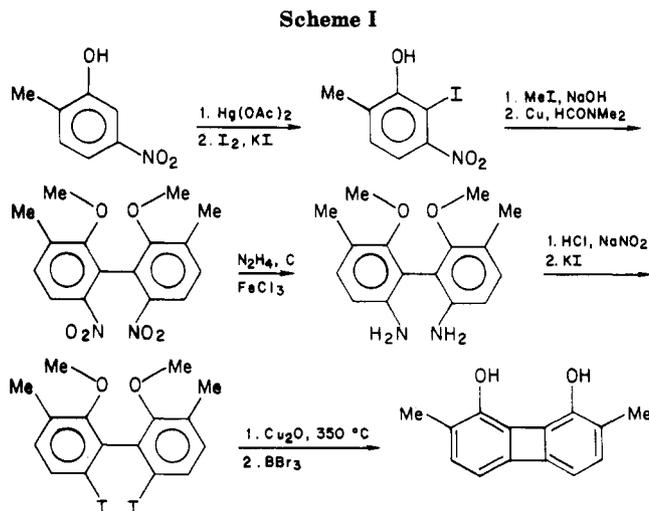
Received May 20, 1985

2,7-Dimethyl-1,8-biphenylenediol has been synthesized from 2-methyl-5-nitrophenol in nine steps. 1,5-Biphenylenediol has been prepared by dimerization of 3-methoxybenzyl, separation of isomers, and demethylation. 8-Methoxy-1-biphenylenol has been made by the partial demethylation of 1,8-dimethoxybiphenylene. Ionization constants ( $\text{p}K_1$  8.04,  $\text{p}K_2$  11.47,  $\text{p}K_1$  8.35,  $\text{p}K_2$  9.97, and  $\text{p}K$  9.15, respectively) have been determined for these compounds and for 1,8-biphenylenediol ( $\text{p}K_1$  8.01,  $\text{p}K_2$  11.00) and 1-biphenylenol ( $\text{p}K$  8.64) by ultraviolet spectrophotometric measurements in aqueous solution.

As part of our study of double hydrogen bonding by 1,8-biphenylenediol<sup>2,3</sup> and its derivatives, we have synthesized some new derivatives of 1-biphenylenol and determined their ionization constants and also the ionization constants of some known 1-biphenylenol derivatives.

The synthesis of 2,7-dimethyl-1,8-biphenylenediol was carried out, as shown in Scheme I, by a method similar to that used previously to synthesize 1,8-biphenylenediol itself.<sup>4,5</sup> The overall yield was 3.9%, based on 6-methyl-3-nitrophenol, similar to the 4.4% of the 1,8-diol itself in nine analogous steps. The previously used method for reduction of the nitro groups by tin and hydrochloric acid was replaced by a hydrazine reduction method.<sup>6</sup>

The 1,5-biphenylenediol was made by a method in which 3-methoxybenzyl is presumably dimerized and the mixture of dimethoxybiphenylenes separated, as shown in Scheme II. The 10% yield of dimethoxybiphenylenes consisted of about 80% 1,5-isomer and 20% 1,8-isomer.



The 8-methoxy-1-biphenylenol was obtained by stopping the cleavage of 1,8-dimethoxybiphenylene by boron tribromide, which was already being carried out as part of the synthesis of 1,8-biphenylenediol, when the maximum amount of a previously unknown intermediate, as measured by TLC, was present.

All the ionization constants were obtained by ultraviolet measurements on aqueous solutions of known concentrations of the 1-biphenylenol derivative of various measured pHs. Most of the aqueous solutions contained buffers and

(1) This research was supported in part by NSF Grant CHE-8114770. Abstracted in part from the Ph.D. Dissertations of David E. Miles and Soonkap Hahn, The Ohio State University, Columbus, OH, 1982 and 1985, respectively.

(2) Hine, J.; Ahn, K.; Gallucci, J. C.; Linden, S.-M. *J. Am. Chem. Soc.* 1984, 106, 7980-7981.

(3) Hine, J.; Linden, S.-M.; Kanagasabapathy, V. M. *J. Am. Chem. Soc.* 1985, 107, 1082-1083.

(4) Baker, W.; Barton, J. W.; McOmie, J. F. W. *J. Chem. Soc.* 1958, 2658-2665.

(5) Blatchly, J. M.; Gardner, D. V.; McOmie, J. F. W.; Watts, M. L. *J. Chem. Soc. C* 1968, 1545-1549.

(6) Hirashima, T.; Manabe, O. *Chem. Lett.* 1975, 259-260.