sulfate and the solvents were removed, whereupon a brown solid (800 mg.) was obtained. The crude diethyl phosphate derivative (800 mg.) in anhydrous tetrahydrofuran (10 ml.) was added to liquid ammonia (100 ml.). Lithium wire (500 mg.) was added in small pieces with stirring. When the metal had dissolved completely, ammonium chloride (1 g.) was added and the mixture was stirred until the ammonia had evaporated. The residue was dissolved in a mixture of chloroform and 5% hydrochloric acid solution. After separating the chloroform layer the aqueous part was again extracted with chloroform and the chloroform solution was washed with 5% sodium hydroxide solution. On removing chloroform, a light brown residue was obtained, and this, on evaporative distillation at 150–170° (bath temperature) and 8 mm., afforded a white crystalline solid, m.p. 83–84°. After crystallization once from petroleum ether, it melted at 89–90°, alone or mixed with an authentic sample of XXVII.

**Isomerization of Methyl Desoxy-*cis*-podocarpate (XXVIII) with Palladium on Charcoal.**—The methyl ester XXVIII (80 mg.) was mixed with palladium on charcoal (80 mg., 10%) in a dehydrogenation tube and heated under nitrogen in a metal bath (preheated to 235°). The temperature was maintained in the range of 235–240° for 1 hr., the tube was then cooled to room temperature, and the mixture was triturated with benzene (10 ml.). It was then poured onto a small column of neutral alumina (3 g.) and washed down with benzene (400 ml.). From the eluate benzene was distilled off under reduced pressure and the product was obtained as a colorless oil. On dissolution in methanol, crystals slowly separated, m.p. 118–120°.

The solid (75 mg.) was mixed with a solution of potassium hydroxide (200 mg.) in water (0.2 ml.) and 1-butanol (2 ml.) and heated under reflux for 10 hr. under nitrogen. It was cooled, diluted with water, and extracted with chloroform. The chloroform solution was washed with water and the solvent was then distilled off. The residue furnished crystals from methanol, m.p. 131–132° (50 mg.). The mixture melting point with an authentic sample of XXIX (m.p. 131–132°) showed no depression. The aqueous alkaline solution from hydrolysis was acidified with dilute hydrochloric acid and extracted with chloroform. The organic extract was washed with water and chloroform was distilled off. The residue was crystallized several times from methanol and this furnished the acid XXXII, m.p. 206°, alone or mixed with an authentic sample.

**Isomerization of Methyl 7-Isopropyldesoxy-*cis*-podocarpate (XXX).**—The *cis* ester XXX (60 mg.), mixed with palladium on charcoal (60 mg., 10%) was heated under exactly the same conditions as before. The product was separated from the catalyst as above, and the colorless oily product slowly afforded crystals, m.p. 76–78°. The whole product was hydrolyzed with 10% aqueous 1-butanolic potassium hydroxide solution as above and the acidic and neutral fractions were separately isolated through extraction with chloroform. The neutral part, on crystallization from methanol, afforded the *trans* ester XXXI (40 mg.) and this melted at 98–99° alone or mixed with an authentic sample (m.p. 98–99°). The acidic fraction furnished crystals (10 mg.), m.p. 155°, and this was found to be identical with XXXIII, through a mixture melting point determination with an authentic sample (m.p. 155°).

**Treatment of Dehydroabietonitrile (XXXIV) with Palladium on Charcoal.**—Dehydroabietonitrile (1 g.) was mixed with palladium on charcoal (1 g., 10%) and heated in a metal bath at 235–240° as before. The product, when eluted through alumina (5 g.) with benzene, crystallized readily, m.p. 84°. This was crystallized once from petroleum ether and the melting point rose to 88° and exhibited no depression in melting point with the starting material, m.p. 88°.

**Acknowledgment.**—Our thanks are due to Dr. P. Dowd, Chemistry Department, Harvard University, for kindly reading the manuscript and to Dr. U. R. Ghatak for helpful discussions during preparation of the manuscript and for interpretation of n.m.r. spectra.

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# Fused Organic Salts. III.[1a] Chemical Stability of Molten Tetra-*n*-alkylammonium Salts. Medium Effects on Thermal $R_4N^+X^-$ Decomposition. $RBr + I^- = RI + Br^-$ Equilibrium Constant in Fused Salt Medium

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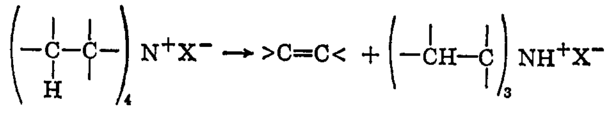
A selected set of low-melting tetra-*n*-alkylammonium salts, $Q^+X^-$ ($X$ = Br, I, SCN, $NO_3$, picrate, $ClO_4$), were shown to be stable during short periods at temperatures just above their freezing points (50–100°), thus demonstrating the feasibility of making meaningful physical measurements in such melts. At 140° four of the salts ($X$ = Br, I, SCN, $NO_3$) decomposed to $RX + R_3N$ and/or olefin $+ R_3NH^+X^-$ to varying degrees. The olefin appears to arise from secondary reaction of $R_3N$ and $RX$. Relative reactivities in the reverse Menschutkin decomposition in a variety of media are compared with the fused salt results and all of the available information is re-evaluated in terms of recent studies of medium effects on anion nucleophilicities. The equilibrium constant for the reaction, $Q^+I^- + n\text{-HexBr} = Q^+Br^- + n\text{-HexI}$, in molten tri-*n*-hexyl-*n*-heptylammonium iodide-bromide ($X_{I^-} \sim 0.97$) was found to be 0.029.

Part IV of this series[1c] describes a collection of low-melting quaternary ammonium salts and provides information on phase relations in binary salt–salt and salt–organic nonelectrolyte systems. Another property of fundamental importance which governs the utility of these melts is their chemical stability. This report describes measurements on the chemical stability of fused quaternary ammonium salts, $Q^+X^-$, containing six common anions. The results help to define the temperature ranges available to decomposition-free experimentation in melts of these materials, and also provide useful information on the chemical reactions involved and some characteristics of the fused salt medium. Closely related to the $Q^+X^-$ decomposition reactions are equilibria of the type $RX' + Q^+X^- \rightleftharpoons RX + Q^+X'^-$; measurements of the equilibrium constant for one such system are included in the present report.

**Fused Salt Decomposition Products.**—Two modes of thermal quaternary ammonium salt decomposition are

$$R_4N^+X^- \longrightarrow RX + R_3N \qquad (1)$$



$$\left(-\overset{|}{\underset{\underset{H}{|}}{C}}-\overset{|}{\underset{|}{C}}-\right)_4 N^+X^- \longrightarrow \,>C{=}C<\, + \left(-CH-\overset{|}{\underset{|}{C}}\right)_3 NH^+X^- \qquad (2)$$

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[1] (a) Part II: J. E. Gordon, *J. Am. Chem. Soc.*, **87**, 1499 (1965); (b) Woods Hole Oceanographic Institution, Woods Hole, Mass. 02543; (c) to be published.

known[2]: the reverse Menschutkin (1)[3,4] and Hofmann (2)[4,5] types. One would expect reactivity in reaction 1 to follow established orders[6-8] of $X^-$ nucleophilicity toward saturated carbon. One might expect reactivity in reaction 2 to follow the order of $X^-$ basicities (approximately $ClO_4^- < I^- < Br^- < NO_3^-, SCN^-$, picrate$^-$),[9,6a] although it is not clear whether bases as weak as the anions under consideration can indeed bring about such an E2 process directly.[4,10]

Table I gives results of analyses for decomposition products performed on melts held for 3 hr. (a) at 401° and (b) at 5° above the melting point. The materials chosen were the lowest melting available representatives of salts of the anions of interest.[1c]

TABLE I

DECOMPOSITION PRODUCTS OF SOME FUSED ORGANIC SALTS

| Material[a] | Temp., °C. | Yield, %, after 3 hr. Olefin | RX | $R_3N$ |
|---|---|---|---|---|
| $Q_{6667}ClO_4$ | 140 | <0.03 | *b* | <0.04[c] |
| $Q_{5555}$Pic | 140 | <0.04 | *b* | <0.04[d] |
| $Q_{6666}NO_3$ | 140 | <0.03 | *b* | 0.08[d] |
| $Q_{5555}SCN$ | 140 | <0.05 | 1.0 | 1.1[d] |
| $Q_{6667}I$ | 140 | 2.2[e] | 4.0 | 2.5[d] |
| $Q_{7777}Br$ | 140 | 9.0[f] | 14 | 17,[c] 18,[c] 15.5[d] |
| $Q_{7777}Br$ (6 hr.) | 140 | 33[f] | 25 | . . . |
| $Q_{6667}ClO_4$ + 0.16 equiv. of $Am_3N$ | 140 | <0.03 | | |
| $Q_{7777}Br$ + 0.17 equiv. of $Am_3N$ | 140 | 9.5[f] | 19 | |
| $Am_3N$ (0.188 mmole) + AmI (0.216 mmole) | 140 | 14[g] | | |
| $Q_{6666}NO_3$ | 74 | . . . | . . . | <0.02[d] |
| $Q_{5555}SCN$ | 55 | <0.035 | <0.2 | <0.02[d] |
| $Q_{6667}I$ | 99 | <0.035 | <0.2 | <0.05[d] |
| $Q_{7777}Br$ | 94 | <0.035 | <0.13 | <0.05[d] |

[a] $Q_{6667}$ = tri-*n*-hexyl-*n*-heptylammonium; $Q_{5555}$ = tetra-*n*-pentylammonium, etc.; Pic = picrate. [b] No new peak observed in vapor phase chromatogram. [c] Procedure A. [d] Procedure B. [e] 1-Hexene + 1-heptene. [f] 1-Heptene. [g] 1-Pentene.

Although no detectable decomposition occurs in 3 hr. (and probably during extended periods) just above the melting point, four of the six salts showed appreciable decomposition at 140°. The results thus validate at least a narrow decomposition-free temperature range for physical measurements in the liquid salt, while emphasizing the desirability of obtaining the lowest melting compounds possible.

**Anion and Medium Effects in Reaction 1.**—The observed order of decreasing $R_4N^+X^-$ stability with respect to $R_3N + RX$ in the molten salt is indeed roughly that of increasing $X^-$ nucleophilicity. The observed reactivity order $Br^- > I^-$ for reaction 1, however, conflicts directly with statements of Goerdeler[11] and Hünig and Baron,[12] both of whom give the order of rate of $Q^+X^-$ decomposition as $I^- > Br^- > Cl^-$ without specifying the medium or citing an experimental source of this information. It is thus desirable to review all of the material available on reaction 1, employing the recently unified picture[7,8,13] of medium effects on relative $X^-$ nucleophilicity as starting point.

According to this view, the innate reactivity sequence toward saturated carbon is $Cl^- > Br^- > I^-$, and this order is observed in dipolar aprotic solvents. In hydroxylic solvents anion solvation *via* hydrogen bonding,[14] which increases in the above order, reverses the nucleophilicity order to $I^- > Br^- > Cl^-$. Finally, in solvents of low dielectric constant where ion association becomes increasingly important in the order $Cl^- > Br^- > I^-$, the anion is deactivated in the ion pair and the nucleophilicity order $I^- > Br^- > Cl^-$ can again result. With this information a predicted reactivity order for reaction 1 can be compared with experiment in several media. This is done in Table II where the available kinetic data for reaction 1 have been supplemented by combining equilibrium constants with kinetic results for the reverse reaction using the relation

$$K^{I^-}/K^{Br^-} = (k_f^{I^-}/k_f^{Br^-})/(k_r^{I^-}/k_r^{Br^-}) \quad (3)$$

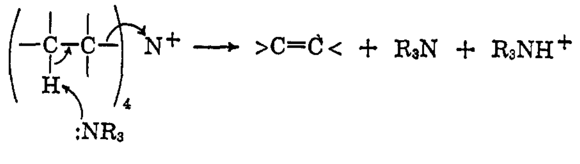
where $k_r$ and $k_f$ represent the reverse and forward rate constants, and $K$ the equilibrium constant for reaction 1. The quotient $K^{I^-}/K^{Br^-}$ reduces to the equilibrium constant for

$$RBr + R_4N^+I^- = RI + R_4N^+Br^- \quad (4)$$

for which Parker[15] has provided some measurements.

Clearly the reactivity order is strongly medium dependent, and this dependence is predictable on the above basis.

**Reaction 2.**—The observed order of olefin production does not correspond to $X^-$ basicity. It appears instead to be coupled with the extent of reaction 1. The ratio of olefin/$R_3N$ increases from 0.64 after 3 hr. to 1.3 after 6 hr. To identify the reaction in which a product of reaction 1 is involved in producing olefin, the effect of $R_3N$ on molten $R_4N^+X^-$ was first tested (Table I). Neither with X = $Br^-$ nor $ClO_4^-$ does the process



appear to provide measurable amounts of olefin.[16] The olefin-forming reaction was found simply to be dehydrohalogenation of RX by $R_3N$ (Table I). Similar results were obtained with RI and $R_3N$ in molten $Q_{6667}$-$ClO_4$ as solvent. This is a known side reaction in the

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(2) A. W. Hofmann, *Ann.*, **78**, 253 (1851).

(3) (a) A. W. Hofmann, *ibid.*, **74**, 117 (1850); (b) *Proc. Roy. Soc.* (London), **10**, 594 (1860); (c) W. Lossen, *Ann.*, **181**, 364 (1876); (d) N. Collie and S. B. Schryver, *J. Chem. Soc.*, **57**, 767 (1890); (e) E. Wedekind and F. Paschke, *Ber.*, **43**, 1303 (1910); (f) E. von Meyer, *Abh. d. matem.-phys. Klasse d. Sächs. Gesellschaft d. Wissenschaften*, **31**, 179 (1908); *Chem. Abstr.*, **5**, 887 (1911); (g) K. von Auwers and W. Mauss, *Ber.*, **61**, 2411 (1928), and previous papers; (h) A. Zaki and H. Fahim, *J. Chem. Soc.*, 270 (1942).

(4) W. Hanhart and C. K. Ingold, *ibid.*, **130**, 997 (1927).

(5) E. D. Hughes, C. K. Ingold, and C. S. Patel, *ibid.*, 526 (1933).

(6) (a) J. O. Edwards, *J. Am. Chem. Soc.*, **76**, 1540 (1954); (b) J. O. Edwards and R. G. Pearson, *ibid.*, **84**, 16 (1962).

(7) S. Winstein, L. G. Savedoff, S. Smith, I. D. R. Stevens, and J. S. Gall, *Tetrahedron Letters*, **No. 9**, 24 (1960).

(8) J. F. Bunnett, *Ann. Rev. Phys. Chem.*, **14**, 281 (1963).

(9) I. M. Kolthoff, S. Bruckenstein, and M. K. Chantooni, Jr., *J. Am. Chem. Soc.*, **83**, 3927 (1961).

(10) C. Harries, *Ber.*, **34**, 300 (1901).

(11) J. Goerdeler in "Methoden der organischen Chemie," Vol. 11/2, E. Müller, Ed., Georg Thieme Verlag, Stuttgart, 1958, p. 633.

(12) S. Hünig and W. Baron, *Ber.*, **90**, 395 (1957).

(13) A. J. Parker, *Quart. Rev.* (London), **16**, 163 (1962).

(14) A. Allerhand and P. von R. Schleyer, *J. Am. Chem. Soc.*, **85**, 1233 (1963).

(15) A. J. Parker, *Proc. Chem. Soc.*, 371 (1961).

(16) This is also the case in excess amine as solvent.[12]

TABLE II

MEDIUM EFFECTS ON REACTIVITY IN THE REVERSE MENSCHUTKIN REACTION

| | | Reactivity sequence | | | |
|---|---|---|---|---|---|
| Medium | Nucleophile | Observed | Source | Predicted | Source |
| Fused salt | $X^-$ | $Br^- > I^-$ | Table I | $Cl^- > Br^- > I^-$ | *a* |
| Dipolar aprotic and nonpolar solvents | $X^-$ and $X^-C^+$ | $Br^- > I^-$ (∼2:1) | Eq. 3<br>$k_r^{I^-}/k_r^{Br^-} = 6.3$[d]<br>$K^{I^-}/K^{Br^-} = 0.08$[f] | $Cl^- > Br^- > I^-$[b] | *a, c* |
| | | $Br^- > I^-$ (∼8:1) | Eq. 3[g] | | |
| Hydroxylic solvents | $X^- \ldots HOR$ | $I^- > Br^- > Cl^-$ (∼15:5:1) | Eq. 3[h] | $I^- > Br^- > Cl^-$ | *a, c* |
| Chloroform solution | $X^- \ldots HCCl_3$ | $I^- > Br^- > Cl^-$ (25:5:1) | *i* | $I^- > Br^- > Cl^-$ | *a, c, j* |
| Solid salt | $X^-$ | $I^- > Cl^-$ | *k* | ? | |

[a] Ref. 7, 13. [b] In this case of reaction of $X^-$ *with its counterion* the innate nucleophilicity and ion association orders reinforce in promoting the indicated reactivity sequence. [c] Ref. 8. [d] For $Et_3N + EtX$ in acetone at 100°.[e] [e] A. Streitwieser, *Chem. Rev.*, **56**, 602 (1956). [f] For MeX in acetone at 25°.[15] [g] The average of $k_r^{I^-}/k_r^{Br^-}$ in benzene (6.8) and acetone (6.3)[e] was compared with $K^{I^-}/K^{Br^-}$ in nitrobenzene.[15] [h] By combination of $k_r$ data for pyridine + $C_6H_5CH_2X$ in 90% aqueous ethanol[e] with equilibrium data[15] for MeX in water. The $k_r$ ratios are nearly constant for solvent variations within the hydroxylic and nonhydroxylic categories. [i] Racemization kinetics of *d*-methylpropylphenylbenzylammonium halides in chloroform at 35° [E. Wedekind, O. Wedekind, and F. Pasche, *Ber.*, **41**, 1029 (1908)]. There is good evidence that the racemization path is reaction 1 [H. von Halban, *Ber.*, **41**, 2417 (1908)]. [j] Ref. 14. [k] Ref. 18.

Menschutkin reaction.[17] Hanhart and Ingold[4] found that $R_4N^+Cl^-$ and $R_4N^+I^-$ fell anomalously between the phenoxide or carbonate and the *m*-nitrophenoxide or acetate in the sequence of relative importance of reaction 2 *vs.* reaction 1. It seems likely that $R_3N$ dehydrohalogenation of RX is also the source of extra olefin in this case.

The relative positions of equilibrium in reaction 1 should be given by equilibrium constants for reaction 4. However, due to reaction 2 the equilibrium condition of $R_4N^+X^-$ with strongly nucleophilic $X^-$ in the fused salt is evidently complete decomposition to olefin + $R_3NH^+X^-$. Only with R = $CH_3$ does the question of equilibrium in reaction 1 become real. This is a case of decomposition of the solid salt without melting for which some information, discussed in the following section, is available.[18]

**$RBr + Q^+I^- = RI + Q^+Br^-$ Equilibrium Constant.**—Table III contains results of measurements of the equilibrium constant for the reaction

$$n\text{-HexBr} + Q_{6667}{}^+I^- \overset{K}{\rightleftharpoons} n\text{-HexI} + Q_{6667}{}^+Br^- \qquad (5)$$

in molten $Q^+I^-$–$Q^+Br^-$ medium. Equilibrium was approached from both directions. The measured equilibrium constant, $K = 0.029$, refers to the medium QI–QBr ($X_{QI} = 0.976 \pm 0.005$); the magnitude of possible medium effects as a function of $X_{QI}$ has not yet been investigated.

TABLE III

EQUILIBRIUM IN THE SYSTEM *n*-HEXI–*n*-HEXBR–QI–QBR AT 100°

| Reactants | Equilibration time, hr. | Measured RI/RBr | $X_{QI}$[a] | $K^b \times 10^2$ |
|---|---|---|---|---|
| QI + RBr | 0.5 | 1.29 | 0.980 | 2.7 |
| QI + RBr | 2 | 1.34 | 0.978 | 3.0 |
| QBr + RI | 1 | 0.951 | 0.971 | 2.7 |
| QBr + RI | 1 | 1.19 | 0.974 | 3.2 |
| | | av. $K = 2.9 \pm 0.2 \times 10^{-2}$ | | |

[a] $X_{QI}$ = mmoles of QI/(mmoles of QI + mmoles of QBr). [b] Equation 5.

This result is to be compared with those of Parker[15] for reaction 4 with butyl halides in nitrobenzene solution at 80°, with methyl halides in acetone at 25°, and with methyl halides in water at 25°, for which $K$ is, respectively, $2 \times 10^{-2}$, $8 \times 10^{-2}$, and 13. By this test $X^-$ is showing similar behavior in the fused salt medium to that encountered in solution in dipolar aprotic solvents. An independent criterion,[1c] more sensitive than this differential $Br^-$–$I^-$ behavior, indicates that anion interactions are in fact smaller in the fused $Q^+X^-$ than in solution in dipolar aprotic solvents. It is natural to identify the shift of equilibrium to the left in reaction 4 on changing from water to dipolar aprotic solvent as primarily the result of loss of stabilizing hydroxylic solvent–$X^-$ interaction, which is greater for $Br^-$ than $I^-$.[13,15] If one anticipates, neglecting all RX and cation interactions, that the change from water to a completely noninteracting medium will increase $\Delta F$ for reaction 4 by the difference in free energy of hydration of $Br^-$ and $I^-$, 8 kcal. mole$^{-1}$,[19] it is evident that the solution in dipolar aprotic solvent and the fused salt alike have realized only about half of the expected differentiation in $Br^-$–$I^-$ stability. Clearly there remain strong anion interactions in these media.

Finally, it is instructive to evaluate approximately the equilibrium constant for the reaction

$$(CH_3)_4N^+I^-(s) + CH_3Cl(g) = (CH_3)_4N^+Cl^-(s) + CH_3I(g) \qquad (6)$$

from the equilibrium dissociation pressures of tetramethylammonium chloride and iodide reported by Smith and Calvert.[18] Assuming ideal gas behavior for $CH_3X$ and $(CH_3)_3N$ and performing a short extrapolation of the $Q^+Cl^-$ data to 240°, the values of the equilibrium constant $K = p^{RX}p^{R_3N}$ ($p$ in atmospheres) for the reaction $R_4N^+X^-(s) = R_3N(g) + RX(g)$ at this temperature are 0.48 and 0.0028 for the chloride and iodide, respectively. The equilibrium constant for reaction 6 is thus $0.0028/0.48 = 5.9 \times 10^{-3}$. Parker's[15] results for the solution analog of reaction 6

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(17) See ref. 11, p. 598.

(18) A. Smith and R. P. Calvert, *J. Am. Chem. Soc.* **36**, 1363 (1914).

(19) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Academic Press Inc., New York, N. Y., 1959, p. 70.

are 1.3 × $10^{-4}$ (nitrobenzene, 80°), 4.7 × $10^{-4}$ (acetone, 25°), and 1.3 (water, 25°).

## Experimental

**Materials.**—Salts were those described elsewhere,[10] recrystallized three or more times and dried at room temperature and $\sim 10^{-4}$ mm. before use. Alkyl halides were commercial materials which were found homogeneous to gas chromatography.

**Fused Salt Decomposition Products.** A.—Salt samples (0.2–0.8 mmole) were heated in a glass-stoppered long-necked flask. After cooling, the salt was dissolved in 5 ml. of glacial acetic acid and the solution was titrated potentiometrically with 0.01 *N* $HClO_4$ in 99.9% dioxane.

B.—Salt samples (0.1–0.2 g.) were sealed in evacuated 3-ml. ampoules. After heating, the ampoules were opened at 0° and the salt was triturated with 2 ml. of pentane and filtered. The solid and ampoule were washed with four more portions of pentane, the filtrates being collected in 7 ml. of acetic acid. The pentane was evaporated from this mixture and the acetic acid solution was titrated with $HClO_4$.

C.—Sample tubes treated as in B were opened at −80° and 0.5 ml. of cyclooctane was added. The pulverized solid was allowed to settle and a 5-μl. sample of the supernatant liquid was chromatographed on a 2.5-m., 25% silicone 702 on 30–60-mesh firebrick column at 170°. Effluent peaks were identified by comparison with authentic specimens and determined by comparison of planimetrically determined peak areas with those given by standard solutions in cyclooctane when measured under the same conditions.

**Equilibrium Constant Measurements.**—The salt or salt mixture (*ca.* 1.0 mmole) and alkyl halide (*ca.* 0.04 mmole) were weighed into glass ampoules, sealed, equilibrated at 100 ± 0.5°, and rapidly quenched so that the salt crystallized instantly. The product was extracted with pure heptane and an aliquot of the heptane solution was analyzed gas chromatographically as described in the preceding section.

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# The Herz Reaction. The Formation and Hydrolysis of Herz Compounds

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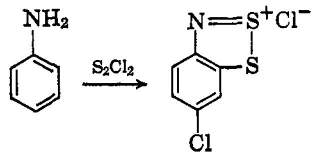
Evidence is given for the time sequence involved in the nuclear chlorination which occurs in certain Herz reactions. The previously unknown parent Herz compound, 1,3,2-benzothiazathiolium chloride, is synthesized and a new method for the synthesis of Herz compounds is given. A convenient method for the preparation and purification of some 3H-1,2,3-benzodithiazole 2-oxides is also present.

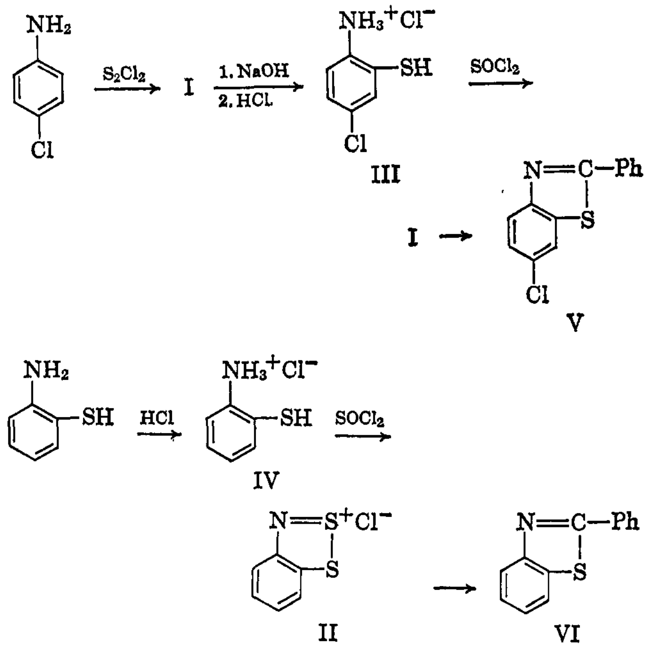
In spite of the fact that the reaction of aromatic primary amines with sulfur monochloride to give substituted 1,3,2-benzothiazathiolium chlorides (Herz compounds) has been known for a long time,[1,2] little is known about the mechanism of the reaction. For example, treatment of aniline with sulfur monochloride leads to the formation of 6-chloro-1,3,2-benzothiazathiolium chloride (I).[3,4] Attempts to alter the conditions of the Herz reaction to obtain this interesting heterocyclic system without the accompanying nuclear chlorination have been unsuccessful.[5,6] Consequently, one of the unresolved problems has been a determination of the point in the reaction sequence when nuclear chlorination occurs. This problem has now been partially answered by the synthesis of the previously unknown parent compound, 1,3,2-benzothiazathiolium chloride (II), and a study of its behavior with sulfur monochloride.



I

It had been suggested that substituted Herz compounds might be made by treating the appropriately substituted *o*-aminothiophenol with thionyl chloride, although no experimental work has ever been reported on this possibility.[7] To test this potential method of synthesis of Herz compounds, the hydrochlorides of 2-amino-5-chlorobenzenethiol (III) and 2-aminobenzenethiol (IV) were synthesized and treated with thionyl chloride in a manner illustrated by Scheme I.

SCHEME I



The conversion of the hydrochlorides to the Herz compounds (I and II) by treatment with thionyl chloride was accomplished in crude yields of 70 and 96%, respectively. Since Herz compounds decompose upon heating and are very difficult to purify, I and II were converted for the purpose of identification to the known

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(1) R. Herz, *Chem. Zentr.*, **4**, 948 (1922).

(2) Cassella and Co., German Patent 360,690 (Oct. 6, 1922).

(3) W. König, *Ber.*, **61**, 2065 (1928).

(4) For further examples of the Herz reaction, see W. K. Warburton, *Chem. Rev.*, **57**, 1011 (1957).

(5) K. J. Farrington and W. K. Warburton, *Australian J. Chem.*, **8**, 545 (1955).

(6) K. J. Farrington and W. K. Warburton, *ibid.*, **9**, 480 (1956).

(7) Weinberg, *Ber.*, **63A**, 117 (1930).