tals of dibenzoyl-D-tartaric acid monohydrate. The solid was removed by filtration, and the filtrate was cooled and made basic with cold 33% potassium hydroxide solution. The alkaline solution was extracted with ether and the ether extracts were dried. The ether was evaporated and the residue was distilled under reduced pressure, yielding 5.1 g. of (−)-octahydropyrrocoline, b.p. 58–59° (18 mm.), n^{20}_D 1.4712, $[\alpha]^{27}_D$ −7.89°.

Anal. Calcd. for $C_8H_{15}N$: C, 76.74; H, 12.08; N, 11.19. Found: C, 76.50; H, 11.96; N, 11.40.

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Partition Studies. VIII. Silver Complexes of Aromatic Amines

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Silver ion reacts like a generalized acid with a variety of olefinic[1,2] and aromatic compounds[3–5] according to the equations

$$Ag^+ + B \overset{K_1}{\rightleftarrows} AgB^+ \qquad (1)$$

$$Ag^+ + AgB^+ \overset{K_2}{\rightleftarrows} Ag_2B^{++} \qquad (2)$$

With nitrogen bases, complexes of the 1:2 type, AgB_2^+, rather than Ag_2B^{++}, are formed.[6,7] This observation was based upon electrometric measurements of solutions in which the ratio $(Ag^+)_{total}/(B)_{total}$ was usually less than unity. For a high value of this ratio, it seemed likely that aromatic amines would form 2:1 complexes because of the possibility that a second silver ion could coördinate with the aromatic nucleus. It was of interest, therefore, to study the argentation of aniline and its methyl-substituted homologs by the distribution method[1,5] in which a high $(Ag^+)_t/(B)_t$ ratio can be conveniently maintained.

To apply the distribution method, partition coefficients were determined in the presence and in the absence of the complexing agent. The k' values recorded in Table I are the partition coefficients for distribution of aniline and its methyl-substituted homologs between cyclohexane and aqueous silver nitrate solutions in which ionic strength was maintained at unity by addition of appropriate amounts of potassium nitrate. The k-values are the partition coefficients of the amines for distribution between cyclohexane and 1 molar potassium nitrate solution.

In all distributions, the silver ion concentration was much greater than the total concentration of amine (0.005 *M*). Under these conditions, the equilibrium constant, K, for the formation of a 1:1 complex exclusively (equation 1) can be calculated by the equation[5]

$$K = (k/k' - 1)/(Ag^+)_t \qquad (3)$$

On the other hand, if the complexing action proceeds partly to the 2:1 stage (equation 2), K is not independent of $(Ag^+)_t$ and equation 4 applies.[2]

$$K = K_1 + K_1K_2(Ag^+)_t \qquad (4)$$

As indicated in Table I, the calculated K values show a marked increase with silver ion concentration, and K was a linear function of the silver ion concentration for all compounds investigated; this was in accordance with equation 4. From the intercepts and slopes of these straight lines, K_1 and K_2[8] were evaluated and are summarized in Table II, together with the known acidic dissociation constants (pK_a values) of the bases.

TABLE I

DISTRIBUTION OF ANILINES BETWEEN CYCLOHEXANE AND WATER IN THE PRESENCE OF SILVER NITRATE AT 25.0°

$(Ag^+)_t$, moles/liter	k	k'	K	k	k'	K	k	k'	K	k	k'	K
		Aniline			*o*-Toluidine			*m*-Toluidine			*p*-Toluidine	
0.00	1.36			5.73			4.84			4.62		
.05		0.54	30.4									
.10		.33	31.2		1.22	37.0		1.10	34.0		0.90	41.3
.20		.17	35.0									
.25		.13	37.9		0.48	43.8		0.43	41.1		.35	48.8
.35		.088	41.2		.32	48.3		.28	46.5		.24	52.2
.50		.054	48.4		.20	55.2		.17	53.3		.15	59.6
.75											.08	71.0
		N-Methylaniline			3,5-Xylidine			2,6-Xylidine				
0.00	25.2			22.0			34.7					
.05												
.10		12.54	10.2		3.77	48.4		5.58	52.2			
.20												
.25		6.50	11.5		1.54	53.1		1.95	67.2			
.35		4.77	12.3					1.22	78.4			
.50		3.28	13.4		0.65	65.7		0.73	93.0			
.75		1.97	15.7		0.37	78.0						

The observed trends in the K_1 and K_2 values appear to be most consistent with the assumption that the first silver ion coördinates with the amino nitrogen and the second with the aromatic nucleus.

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[1] S. Winstein and H. J. Lucas, THIS JOURNAL, **60**, 836 (1938).

[2] F. R. Hepner, K. N. Trueblood and H. J. Lucas, *ibid.*, **74**, 1333 (1952).

[3] L. J. Andrews and R. M. Keefer, *ibid.*, **72**, 3113 (1950); **72**, 5034 (1950); **73**, 5733 (1951).

[4] P. L. Nichols, *ibid.*, **74**, 1091 (1952).

[5] C. Golumbic and S. Weller, *ibid.*, **74**, 3739 (1952).

[6] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941, p. 298.

[7] R. J. Bruehlman and F. H. Verhoek, THIS JOURNAL, **70**, 1401 (1948).

[8] For a discussion of the relation between these constants and the true thermodynamic equilibrium constants see ref. 2.

TABLE II

EQUILIBRIUM CONSTANTS FOR ARGENTATION AND IONIZATION OF ANILINES AT 25.0°

Amine	K_1	K_2	pK_a
Aniline	27.6	1.45	4.62[a]
o-Toluidine	32.4	1.40	4.43[a]
m-Toluidine	29.2	1.68	4.71[a]
p-Toluidine	36.8	1.24	5.12[a]
3,5-Xylidine	43.0	1.09	4.9[b]
2,6-Xylidine	41.6	2.49	4.1[b]
N-Methylaniline	10.0	0.80	4.78[a]

[a] N. F. Hall, THIS JOURNAL, **52**, 5115 (1930). [b] Ref. 14.

Thus, the increase in K_1 values for the homologous series, aniline < toluidines < xylidines, is that anticipated from the known base-strengthening action of nuclear methyl substituents. However, a comparison between K_1 and pK_a values must take into account the different steric requirements of the anilinium[9] and silver ions.[10] *o*-Methyl substituents markedly decrease the basicity of aniline relative to hydrogen ion but have no pronounced effect relative to the silver ion as an acid; the reverse appears to be true with N-methyl substituents.

The coördination of silver ion with the benzenoid nucleus is also influenced by steric and polar factors. The more widely spaced a pair of substituents is around the ring, the greater is the steric hindrance to coördination.[10] On this basis, it is understandable that *p*-toluidine and 3,5-xylidine have the lowest K_2 values in the toluidine and xylidine series, respectively.

It is also possible that the attachment of the first silver ion decreases the basicity of the ring by resonance inhibition in a manner analogous to the effect of N-alkyl substituents on the base strength of aniline.[9] This may account for the fact that the K_2 values, in particular, that of N-methylaniline, are lower than those observed in the argentation of corresponding benzenoid hydrocarbons.[3]

Information of the type given in Table I is helpful in determining whether complex formation can be utilized to enhance separation of mixtures of compounds by fractional extraction procedures.[11,12] A convenient measure of the separability of compounds is the β-value or ratio of partition coefficients.[13] When 1:1 complex formation occurs, the β-value, k'_c/k'_d for a pair of compounds (in the limit of high concentration of complexing agent), is given by the equation

$$k'_c/k'_d = k_cK_d/k_dK_c \qquad (5)$$

where k_c and k_d represent the partition coefficients of the uncomplexed compounds, and K_c and K_d are the complex formation constants.[5] Application of this relationship to the data of Table I shows that in some instances the complexing action aids and in others hinders separation. Thus, the β-value for a mixture of *o*- and *m*-toluidine is slightly decreased by complex formation, whereas that of a mixture of aniline and N-methylaniline is increased by a factor of almost 3.

Experimental

Materials and Procedure.—The source and purity of the aromatic bases are recorded elsewhere.[14]

The procedure for distribution of the bases is the same in all details as that given in the previous paper of this series,[5] except that the concentration of the initial solutions of the amines was 0.005 *M*. The establishment of equilibrium was checked by the procedure of Barry, *et al.*,[15] in which the partition coefficients were measured after application of known numbers of equilibrations. It was found that equilibrium was established after only ten or twenty equilibrations. The data of Table I are, however, based on measurements after 100 to 200 equilibrations.

Acknowledgment.—The author is indebted to Dr. H. C. Brown for valuable suggestions and to George Goldbach for technical assistance.

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The Preparation of Methylthiazoles

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The method most generally applicable to the synthesis of alkyl thiazoles involves the reaction of α-halocarbonyl compounds with thioamides. The preparation and purification of the thioamides (from the amide and phosphorus pentasulfide) are sometimes difficult and the yields are generally very poor.[1] A modification introduced by Hromatka[2] avoids isolation of the thioamide. It consists in heating a mixture of the stoichiometric quantities of amide, phosphorus pentasulfide and the α-halocarbonyl compound. By this method Schwarz[3] has prepared 2,4-dimethylthiazole in 45% yield by the reaction of five moles of acetamide, one mole of phosphorus pentasulfide and five moles of chloroacetone in benzene. Ganapathi and Venkataraman have prepared this compound[4] and several other methylthiazoles by this method.

Since the yields reported in the syntheses of the methylthiazoles were not too high, the methods used were tedious and difficult to control and large quantities of these substances were required for investigations in the thiazole series, attempts were made to improve the methods of synthesis. Previous workers have assumed that the conversion of acetamide and formamide to the thioamide was quantitative, otherwise no attempt would have been made to react the stoichiometric quantity of haloketone or aldehyde. It is quite obvious, however, on inspection of the reaction mixture, that much tar is produced and that some of the phosphorus pentasulfide remains unreacted. It therefore seemed impractical to use the stoichiometric

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