

the addition was completed, the Dry Ice trap was replaced with another and the system was evacuated at 100 mm. pressure while the reaction vessel was heated to 90°.

The first fraction was washed with 3 portions of cold water, dried over Drierite and then filtered to give 60 g. (38% yield) of 1-bromo-1-propene, b.p. 55–55.2°/708 mm., which was 99% *cis* isomer, before distillation, according to vapor phase chromatographic analysis.⁹

The second fraction was treated in the same manner to give an additional 60 g. (38% yield) of 1-bromo-1-propene. The product consisted of 96% *cis*- and 4% *trans*-1-bromo-1-propene as determined by vapor phase chromatographic analysis.⁹ The total yield of 1-bromo-1-propene was 76%.

Preparation of Propene-d-1. Fifty g. (0.41 mole) of 1-bromo-1-propene (98% *cis* isomer) was added to 10 g. (0.41 mole) of magnesium in 250 ml. of dry tetrahydrofuran in a flask protected from atmospheric moisture and provided with means for distillation. When all the magnesium had reacted, 25 ml. of tetrahydrofuran was distilled out to remove any propene which might have been present. Receivers were changed and 17 ml. of 99.8% deuterium oxide was added dropwise to the stirred Grignard solution. The evolved gas was trapped in a Dry Ice-acetone trap to give 12 g. (70% yield) of propene-d-1. The propene-d-1 contained a small amount of tetrahydrofuran. A sample was purified by gas chromatography⁹ and parent peak analysis on the mass spectrometer indicated that it was at least 99% mono-deuterated propene.

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(9) The analysis was performed by Charles M. Drew of this laboratory.

The Reaction of Oxalyl Chloride with Amine Hydrochlorides

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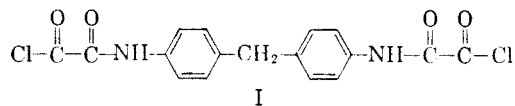
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Stolle¹ successfully prepared oxamic acid chlorides from *N*-substituted anilines by reaction with oxalyl chloride. However, primary aromatic amines and oxalyl chloride gave only oxamides under similar conditions. Several patents² show that the oxamic acid chlorides of certain primary aromatic amines could be prepared by treating the amine hydrochlorides with oxalyl chloride, either in excess oxalyl chloride, or in an inert diluent.

This latter method has now been found applicable to the synthesis of 4,4'-(diphenylmethane)-bis-oxamic acid chloride (I). Good yields of I could be obtained when the dihydrochloride of 4,4'-diaminodiphenylmethane was heated under reflux with excess oxalyl chloride for 12 hours. Poorer yields were obtained when shorter reflux times were used.

(1) R. Stolle, *Ber.*, **46**, 3915 (1913); R. Stolle, R. Bergdoll, M. Luther, A. Auerhahn, and W. Wacker, *J. prakt. Chem.*, **128**, 1 (1930).

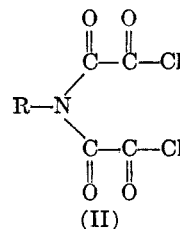
(2) I. G. Farben A-G., Brit. Patent 282,891, Sept. 30, 1926; I. G. Farben A-G., Ger. Patent 463,140, July 5, 1928; J. Haller, U. S. Patent 1,685,698, Nov. 26, 1926.



It was found that I reacted readily with ethanol to give the diester. This was shown to be identical to the diester obtained by reaction of 4,4'-diaminodiphenylmethane with diethyl oxalate by comparison of their infrared spectra and melting points, and no depression in the mixture melting point.

Surprisingly, the dihydrochlorides of *m*-phenylenediamine, piperazine, and *trans*-2,5-dimethylpiperazine were found to be unreactive towards oxalyl chloride. It is felt that this is probably due to the insolubility of these hydrochlorides as opposed to that of 4,4'-diaminodiphenylmethane, which appears to dissolve to some extent at the beginning of the reaction.

In looking for a possible extension of this reaction it was noted that Bornwater³ had reacted methylamine hydrochloride with oxalyl chloride and obtained *N,N'*-dimethyltetraketopiperazine. It appeared likely from our experience that an intermediate in this synthesis might be II (R = CH₃). This could then react with another molecule of amine hydrochloride to form the tetraketopiperazine.



This work indicates that this is indeed the case. A substantial yield of a hygroscopic, hexane soluble diacid chloride was obtained when a mixture of ethylamine hydrochloride and a large excess of oxalyl chloride was heated at reflux for 50 hr. Though the elemental analysis of the product, *N*-ethylloximidic acid chloride⁴ (II; R = C₂H₅), did not agree with the theoretical, that of its di-*N*-methylanilide derivative did. The infrared spectrum of the acid chloride was consistent with what would be expected of a compound having the structure of II.

EXPERIMENTAL⁵

4,4'-Diaminodiphenylmethane dihydrochloride. Fifteen g. of 4,4'-diaminodiphenylmethane dissolved in 350 ml. of anhydrous ether was treated with dry hydrogen chloride for 5 hr. whereupon the colorless, solid product precipitated. This was filtered, washed twice with 300-ml. portions of ether, and dried in a desiccator under vacuum. The dry weight was 19.7 g. (96%), m.p. 282° (dec.) [reported,⁶ m.p. 285° (dec.)].

(3) J. Th. Bornwater, *Rec. trav. chim.*, **31**, 105 (1912).

(4) We are assigning the name oximidic acid to the structure HO₂CCONHCOCO₂H.

(5) All melting points are uncorrected.

4,4'-(Diphenylmethane)bisoxamic acid chloride (I). To 99.3 g. (0.78 mole) of oxalyl chloride was added 10.0 g. (0.037 mole) of 4,4'-diaminodiphenylmethane dihydrochloride in one portion with stirring. The heterogeneous mixture was heated at reflux with stirring for 12 hr. in a dry atmosphere. After removal of the excess oxalyl chloride at reduced pressure with gentle heating, the residual solid was dissolved in about 3 l. of dry, ethanol-free chloroform. The almost clear solution was filtered to remove some fine particles of unchanged dihydrochloride and evaporated on the steam bath to about 500 ml. At this concentration a large amount of yellow, crystalline solid was present. After cooling to room temperature, the yellow needles were filtered off in a dry-box under a dry nitrogen atmosphere, weight 9.9 g. (71%), m.p. 165–167° (dec.).

Anal. Calcd. for $C_{17}H_{12}O_4N_2Cl_2$: C, 53.85; H, 3.19; O, 16.88; N, 7.39; Cl, 18.70. Found: C, 52.65, 52.64; H, 3.08, 3.17; O, 17.0, 16.8; N, 7.16, 7.13; Cl, 19.7, 20.0.

Diethyl 4,4'-(diphenylmethane)bisoxamic acid. To 73.7 g. (0.505 mole) of diethyl oxalate warmed to about 30° was added 10.0 g. (0.0505 mole) of 4,4'-diaminodiphenylmethane with stirring. The solution was heated under reflux for 1.5 hr., then allowed to cool to room temperature. The solid was filtered and dried in a vacuum oven at 20 mm. pressure and 60°. The weight of tan colored product was 17.6 g. (88%), m.p. 150–153°. Recrystallization from ethanol gave colorless needles, m.p. 153–153.5°.

Anal. Calcd. for $C_{22}H_{20}O_4N_2$: C, 63.3; H, 5.60; N, 7.05; O, 24.1. Found: C, 63.28, 63.35; H, 5.83, 5.77; N, 6.94, 6.96; O, 23.9, 24.0.

The diethyl ester was also obtained by using chloroform containing ethanol as recrystallizing medium for 4,4'-(diphenylmethane)bis-oxamic acid chloride. It was obtained as colorless needles (from *n*-hexane/chloroform) in 91% yield, m.p. 152–152.5°. The infrared absorption spectra and mixed melting point of these two samples showed them to be identical.

N-Ethylloximidic acid chloride (II; R = C_2H_5). To 158.4 g. (1.25 mole) of oxalyl chloride protected from the atmosphere by calcium chloride tubes was added 5.0 g. (0.061 mole) of ethylamine hydrochloride with stirring. The mixture was heated at reflux for 50 hr., then the excess oxalyl chloride was removed at reduced pressure. The solid residue was dissolved in a chloroform/*n*-hexane (3/1) mixture and the chloroform boiled off leaving a small amount (100 mg.) of tan crystals, m.p. >220° which showed a negative silver nitrate test. This is believed to be *N,N'*-diethyltetraketopiperazine.

After filtration of this high melting solid the brown filtrate was evaporated to about 80 ml. and allowed to cool in a dry-box. A large amount of tan needles formed which were filtered. These were dried in a vacuum desiccator and the dry weight was 8.0 g. (77%). It was recrystallized from *n*-hexane giving tan needles, m.p. ~85–90°. It showed an immediate positive silver nitrate test and the infrared spectrum was consistent with the structure proposed.

Anal. Calcd. for $C_8H_{10}O_4NCl_2$: C, 31.88; H, 2.23; N, 6.20; Cl, 31.38. Found: C, 32.1, 32.5; H, 2.71, 2.84; N, 6.25, 6.03; Cl, 28.2, 27.5.

The di-*N*-methylanilide was prepared by adding a large excess of *N*-methylaniline to a chloroform solution of the acid chloride. This had a melting point of 118.5–119.5°. Two crystallizations from aqueous ethanol gave colorless crystals, m.p. 132–133°.

Anal. Calcd. for $C_{22}H_{21}O_4N_3$: C, 65.38; H, 5.76; O, 17.4; N, 11.44. Found: C, 65.32, 65.32; H, 5.81, 5.76; O, 17.4, 17.6; N, 11.23, 11.25.

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(6) C. Eberhardt and A. Welter, *Ber.*, 27, 1811 (1894).

Acid Dissociation Constants and Copper Chelate Stability Constants of *N*-Aralkylethylenediamines

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Although the proton and copper(II) complexes of ethylenediamine and its *N*-alkyl-derivatives have been reported,^{2–6} no such data is available for the *N*-aralkylethylenediamines.

N-alkylation of ammonia⁴ leads to an increase in basicity or to stronger proton complexes. Since increased basicity generally produces increased complex stability in a given series of ligands enhanced stability of metal-amine complexes is expected. This reasoning holds true in the case of primary amines but not in the case of secondary or tertiary amines wherein the increased basicity due to *N*-alkyl substitution is simultaneously accompanied by an increase in steric interference and lower stability.³ The same behavior exists in the *N*-aralkylethylenediamines which form weaker metal complexes than does ethylenediamine. The observed order of complex stability: ethylenediamine > *N*-methylethylenediamine > *N*-ethylethylenediamine > *N*-isopropylethylenediamine is the reverse of the order of *pK_a* values (Table II). The effect of steric interference, absent in the proton complexes, becomes more pronounced as R increases in size. It, therefore, became of interest to examine the effect of *N*-monoaralkyl substitution on the proton and copper complexing ability of ethylenediamine.

The acid dissociation constants of the dihydrochlorides of *N*-benzylethylenediamine, *N*-(β -phenethyl)ethylenediamine and *N*-(*p*-methylbenzyl)ethylenediamine, together with the stability constants of their copper(II) complexes at 25° in 0.1M KCl have been determined and are reported here.

EXPERIMENTAL

Reagents. The *N*-aralkylethylenediamines were prepared by direct condensation of the appropriate aralkyl chloride with ethylenediamine in a five to one molar ratio at 85–90° for 4 to 6 hr. The products were liberated from their hydrochloride salts by adding a slight excess of 30% sodium hydroxide solution to the hot reaction mixture and stirring for 1 hr. The aqueous phase was removed and the remaining organic phases dried with solid KOH followed by metallic

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- (2) J. Bjerrum, *Chem. Revs.*, 46, 381 (1950).
- (3) F. Basolo and R. K. Murmann, *J. Am. Chem. Soc.*, 74, 2373 (1952).
- (4) R. N. Keller and L. J. Edwards, *J. Am. Chem. Soc.*, 74, 2931 (1952).
- (5) D. H. Everett and B. R. W. Pinsent, *Proc. Roy. Soc. (London)*, 215, A, 417 (1952).
- (6) H. Irving and M. Griffiths, *J. Chem. Soc.*, 213 (1954).