hydrogen had ceased, and was then refluxed for three hours. The diethyl ether was removed by distillation and the residue in the reaction flask was slowly heated to 250° and maintained at this temperature for four hours. During this stage of the reaction efficient operation of the condenser is essential, for the product may be lost in the stream of hydrogen that is produced. At this time the reaction flask was made to communicate to an oil pump through a trap maintained at −196°. The volatile reaction products were distilled from the flask and condensed in the trap. This trap was then removed from the reaction system, attached to a vacuum apparatus, and the product purified by fractional condensation at −45°. A yield of 0.95 g., 98%, as calculated from equation (3), was obtained.

(b) **Procedure B.**—Monomethylammonium chloride, 16.5 g., and 5.3 g. of lithium borohydride were mixed in a 500-cc. reaction flask arranged as in the former experiments. di-*n*-Hexyl ether, 125 cc., previously dried over sodium hydride, was slowly added through the dropping funnel. After the initial reaction had ceased, the mixture was refluxed for half an hour. The apparatus was arranged for distillation and the mixture was distilled until the products boiling below 134° were collected. The crude product was transferred to a vacuum apparatus and purified by fractional condensation at −45°. A yield of about 7 g., or 70%, was obtained.

(c) **Identity of Product.**—The product was identified[5,6] by its boiling point, 132° (obs. 132–133°), its melting point, −9° (obs. −8 to −7.5°), and by its vapor pressure, 27 mm. at 37° (obs. 28 mm.), 163 mm. at 85° (obs. 158 mm.).

Acknowledgments.—The authors wish to express their gratitude to Mr. Riley Schaeffer and to Mr. M. Berger who assisted in several experiments.

Summary

A simple method for the preparation of N-dimethylaminoborine, trimethylamineborine and N-trimethylborazole by the reaction of lithium borohydride with the appropriate alkylamine chloride is described.

(5) H. I. Schlesinger, D. M. Ritter and A. B. Burg, THIS JOURNAL, **60**, 1297 (1938).

(6) E. Wiberg, K. Hertwig and A. Bolz, *Z. anorg. Chem.*, **236**, 177 (1938).

CHICAGO, ILL. RECEIVED DECEMBER 8, 1948

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ARMOUR AND COMPANY]

The Effect of Inorganic Electrolytes upon the Conductivity of Aqueous Solutions of Dodecylammonium Chloride[1]

BY A. W. RALSTON, D. N. EGGENBERGER AND F. K. BROOME

The general effect of the presence of inorganic electrolytes in enhancing the colloidal properties of colloidal electrolytes is well recognized and reference to some of the prior work upon this subject has been given in our former paper.[1a] In our previous work, which was also concerned with the effect of inorganic electrolytes upon the electrical conductivity of aqueous solutions of dodecylammonium chloride, an attempt was made to compare the effects at similar specific conductivities and, as a consequence, the concentrations of inorganic electrolytes varied over a wide range. Although our results were in substantial agreement with those expected from previous work, the procedure employed led to the masking of several significant facts. The present paper constitutes an extension of our former work upon this subject and compares the effects of various salts and acids at similar concentrations upon the electrical conductivity of aqueous solutions of dodecylammonium chloride.

Experimental

The dodecylammonium chloride was of the same quality as that used in our former work.[2] The conductivities were determined in the manner and with the equipment previously described.[3] The calculation of the conductivity by difference was similar to that employed previously.

Results and Discussion

Figure 1 compares the conductivity of dodecylammonium chloride in pure water with its conductivity by difference in 0.0025, 0.005, 0.01 and 0.02 *N* sodium chloride solutions. It is apparent that progressive increases in the concentration of sodium chloride lower the conductivity attributable to the colloidal electrolyte and materially decrease its critical concentration. A similar effect was noted for 0.0025, 0.005, 0.01 and 0.02 *N* barium chloride solutions, Fig. 2.

In our previous work[1a] concerned with the effect of the presence of hydrochloric acid upon the conductivity of aqueous solutions of dodecylammonium chloride, the conclusion was drawn that although the presence of hydrochloric acid materially lowers the equivalent conductivity it has only a negligible effect upon the concentration at the critical point. Figure 3 shows this latter conclusion to be in error, since the presence of hydrochloric acid lowers both the conductance and the concentration of colloidal electrolyte at the critical point.

The effect of sodium chloride, barium chloride or hydrochloric acid upon aqueous solutions of dodecylammonium chloride may be attributed to two factors, which are, first, the depression in the ionization of the colloidal electrolyte caused by the increase in the common chloride ion and second, the salting-out effect of the strong electrolyte. Randall and Failey[4] have published

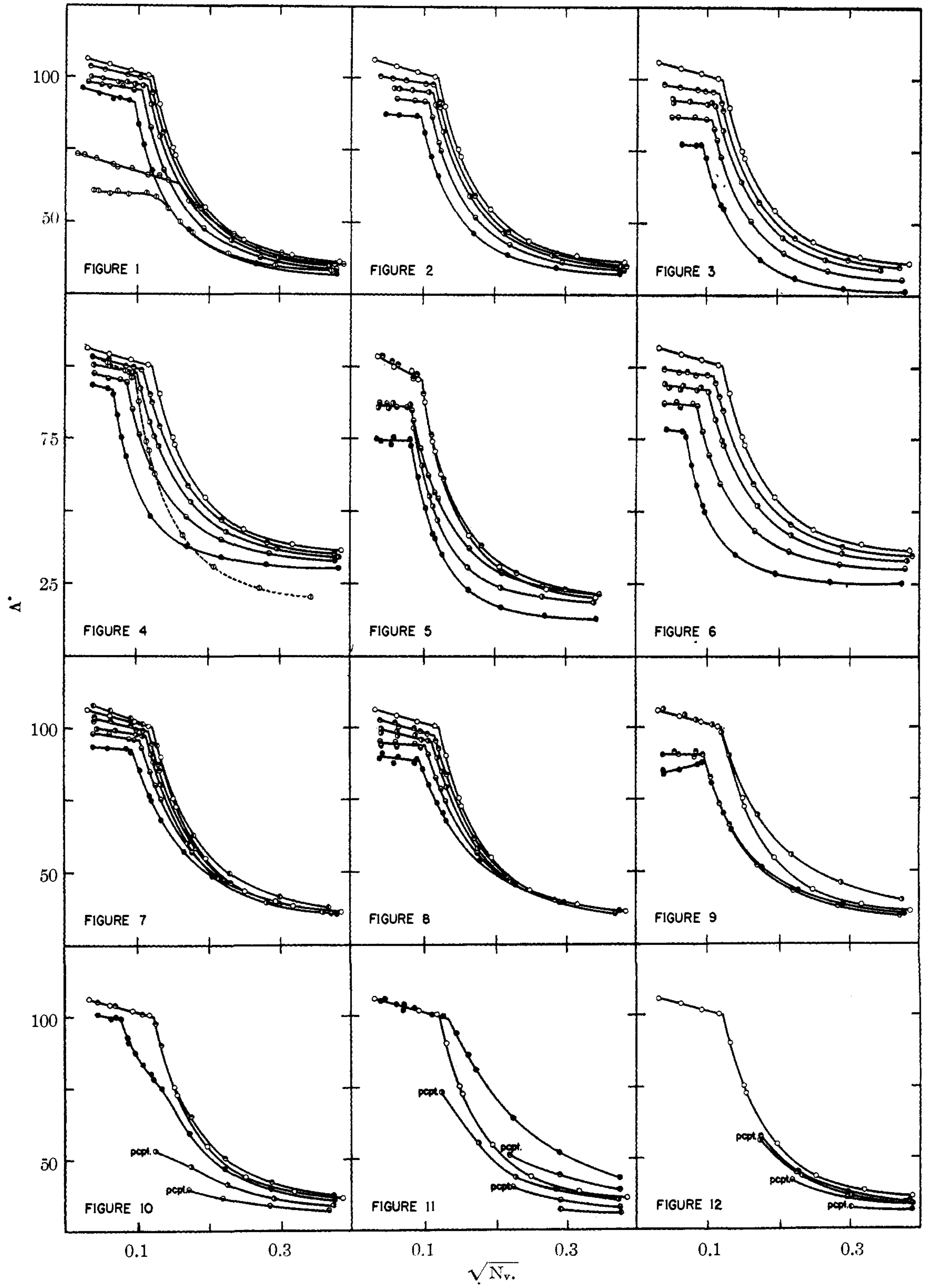
(1) Presented in part before the Colloid Division, 114th Meeting, American Chemical Society, Portland, Oregon, September, 1948.

(1a) Ralston and Eggenberger, THIS JOURNAL, **70**, 980 (1948).

(2) Ralston and Eggenberger, *ibid.*, **70**, 436 (1948).

(3) Ralston, Hoerr and Hoffman, *ibid.*, **64**, 97 (1942).

(4) Randall and Failey, *Chem. Revs.*, **4**, 285 (1927).



Figs. 1-12.—Conductances by difference at 30° (see table on facing page):

the relative salting-out order of ions, and of the positive ions studied, sodium was stated to have the greatest salting-out effect and hydrogen the least. Since hydrochloric acid has a greater

Fig.	Dodecyl ammonium	Soln. of	Concentrations, *N*							
			○	◓	◑	◒	●	◐	⊖	⦶
1	Chloride	NaCl–(MeOH)*	0	0.0025	0.005	0.01	0.02		25 v.%*	0.02 + 25 v.%*
2	Chloride	$BaCl_2$	0	0.0025	0.005	0.01	0.02			
3	Chloride	HCl	0	0.0025	0.005	0.01	0.02			
4	Chloride	$NaNO_3$	0	0.0025	0.005	0.01	0.02			Nitrate
5	Nitrate		..	HAc	NaCl	NaAc	HCl			
			0	0.02	0.02	0.02	0.02			
6	Chloride	HNO_3	0	0.0025	0.005	0.01	0.02			
7	Chloride	$Acetate^-$	..	Na^+	Na^+	Na^+	Na^+	H^+		
			0	0.0025	0.005	0.01	0.02	0.02		
8	Chloride	$CaAc_2$	0	0.0025	0.005	0.01	0.02			
9	Chloride	$Formate^-$	..	Na^+	H^+		Ca^{++}			
			0	0.02	0.02		0.02			
10	Chloride	$Succinate^{--}$	..	H^+	Na^+	Na^+	Na^+			
			0	0.0025	0.01	0.02	0.0025			
11	Chloride	$Tartrate^{--}$	..	Na^+,H^+	Na^+	Na^+	H^+	Na^+		
			0	0.02 ea.	0.0025	0.01	0.02	0.02		
12	Chloride	$Sulfate^{--}$	..	H^+	Na^+	Na^+	H^+	Na^+		
			0	0.0025	0.0025	0.005	0.01	0.01		

depressant effect than sodium chloride upon the equivalent conductivity of dodecylammonium chloride, it appears that factors other than the salting-out properties of the inorganic electrolyte are involved.

It is well established that electrolytes not possessing an ion in common with a colloidal electrolyte frequently have effects upon its colloidal behavior equal to or even greater than the effects of those which do possess a common ion. This is explainable by reason of the equilibrium set up between the long-chain ion and the two oppositely charged ions since, as a consequence, both these ions are common to the components of the micelles. Figure 4 compares the conductivity of dodecylammonium chloride in pure water with its conductivity by difference in 0.0025, 0.005, 0.01 and 0.02 *N* sodium nitrate. The presence of this electrolyte reduces the conductivity of dodecylammonium chloride to an extent comparable with the lowering produced by sodium chloride but the reduction in the critical concentration is significantly greater. The salting-out property of the nitrate ion has been stated[4] to be less than that of the chloride ion so that it is evident that the reduction in the ability of the solvent to hold long-chain ions in solution is only one of the factors contributing to the observed effect of electrolytes upon the solution behavior of dodecylammonium chloride. Nitric acid (Fig. 6) has an effect comparable with that of hydrochloric acid in reducing the conductivity of dodecylammonium chloride; however, its influence upon the critical point is similar to that of sodium nitrate.

The concentration of dodecylammonium chloride at the critical point in the presence of sodium chloride, barium chloride, hydrochloric acid, sodium nitrate and nitric acid plotted against the square root of the normality of inorganic electrolyte is shown in Fig. 13. These curves show conclusively that for these two series of electrolytes the position of the critical point of dodecylammonium chloride is influenced only by the nature and concentration of the anion of the added electrolyte and is independent of the nature and concentration of the cation. These results are in agreement with the findings of Corrin and Harkins[5] that the depression of the critical point is related only to the nature and concentration of the ion opposite in charge to that on the colloidal aggregate.

These observations must have a logical explanation. It is, however, possible that the examples chosen by the several investigators have been fortuitous and that certain limitations should be placed upon generalizations concerned with the effect of electrolytes upon colloidal electrolytes.

At the critical point the undissociated molecules of the colloidal electrolyte are solubilized by the associated ions, thus accounting for the rapid decrease in the equivalent conductivity and the abnormal increase in the transference value of the colloidal ion. In the present paper it is shown that the critical point is lowered to the same extent by equivalent concentrations of sodium and barium chlorides and of hydrochloric acid, thus indicating that all chlorides have similar effects. On the other hand, equivalent concentrations of sodium nitrate and nitric acid also have similar effects which are substantially greater than those of the chlorides. When a nitrate is added to a solution of dodecylammonium chloride the following equilibrium is set up

$$C_{12}H_{25}NH_3Cl + XNO_3 \rightleftharpoons C_{12}H_{25}NH_3NO_3 + XCl$$

The colloidal phenomenon is essentially concerned with the relative concentrations of dodecylammonium chloride and dodecylammonium nitrate, which are influenced by the concentrations of chloride and nitrate ions and are independent of the nature of the cation of the added salt. If the nitrate is less soluble than the chloride the

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[5] Corrin and Harkins, THIS JOURNAL, **69**, 683 (1947).

equilibrium will be greatly in its favor. Solubilization of a less-water-soluble nitrate will take place at a lower concentration than that of a more-soluble chloride, and thus the critical concentration would occur at a lower concentration.

It has formerly been our opinion that the critical concentrations of compounds of similar structure are a function of the chain lengths and are independent of the nature of the gegenion. However, if the above explanation of the relative effects of chlorides and nitrates is correct it requires that the critical concentration of dodecylammonium nitrate in pure water be lower than that of dodecylammonium chloride, which certainly means that the critical point is influenced by the nature of the gegenion. Figure 4 shows that the critical concentration of dodecylammonium nitrate is materially lower than that of the corresponding chloride.

The above considerations are predicated upon the assumption that the salt formed between the long-chain ion and the oppositely charged ion of the added electrolyte is less soluble and has a lower critical concentration than the original colloidal electrolyte. The alternate case exists in which a more-soluble colloidal electrolyte is formed. Studies of the systems which dodecylammonium chloride[6] and dodecylammonium acetate[7] form with water indicate the latter salt to be more soluble. As a consequence, the partial conversion of dodecylammonium chloride to its acetate by the addition of a soluble acetate to an aqueous solution of dodecylammonium chloride should be accompanied by an increase in the water solubility of the colloidal electrolyte. The effect upon the critical concentration would be due essentially to the salting-out properties of the added salt and to an increase in the concentration of an ion common to the components of the micelles. A previous investigation[1a] of the effects of metallic acetates and acetic acid upon the equivalent conductivity of dodecylammonium chloride showed that the presence of metallic acetates reduces the critical concentration, whereas very material additions of acetic acid are without apparent influence.

The equivalent conductivity of dodecylammonium chloride in pure water compared with its conductivity by difference in 0.0025, 0.005, 0.01 and 0.02 *N* sodium acetate and also in 0.02 *N* acetic acid is shown in Fig. 7. It will be noted that the conductivity by difference and the critical concentration are progressively lowered in the presence of increasing concentrations of sodium acetate. The position of the critical point is almost identical with that found in the presence of equal concentrations of sodium chloride. The presence of 0.02 *N* acetic acid, however, increases the equivalent conductivity slightly and has no effect upon the critical concentration. Figure 8 shows that the effect of the presence of calcium acetate upon the critical concentration is identical with that of sodium acetate.

Formates have an effect similar to that of the acetates. The equivalent conductivity and critical concentration are lowered in the presence of 0.02 *N* sodium or calcium formate (Fig. 9), whereas 0.02 *N* formic acid raises the equivalent conductivity and is without influence upon the position of the critical point.

The fact that metallic acetates and formates reduce the critical concentration, whereas the corresponding acids are without effect, presents an apparent contradiction to the generalization that the nature of the anion is without influence. On the other hand, both hydrochloric and nitric acids have effects identical with those of their salts. Undoubtedly, the explanation resides in the fact that weak acids form molecular complexes with dodecylammonium salts. Such complexes are evidently solubilized to an extent comparable with that of the dodecylammonium salt and their formation serves to remove the weak acid from solution. The formation of two stable molecular compounds between octadecylamine and acetic acid has been previously demonstrated.[8] The present conductometric study indicates that such complexes are not present in aqueous solutions of dodecylammonium chloride and metallic salts or strong acids.

Figure 5 shows the conductivity by difference of dodecylammonium nitrate in 0.02 *N* sodium chloride, hydrochloric acid, sodium acetate and acetic acid. Their effects parallel those previously observed with dodecylammonium chloride, the salts and strong acids reducing the critical concentration, whereas the weaker acid is without effect.

It is well known that most dodecylammonium salts of polyvalent anions possess very limited solubilities in water. The effect of inorganic electrolytes containing these ions upon the electrical properties of aqueous solutions of dodecylammonium chloride is of interest, since the dodecylammonium ion will be largely converted to a difficultly soluble compound. Figure 10 shows that systems containing dodecylammonium chloride in 0.01 and 0.02 *N* sodium succinate precipitate at low concentrations of dodecylammonium chloride. It is evident that the difficultly water-soluble dodecylammonium succinate is solubilized by the micelles present in high concentrations of dodecylammonium chloride, but that reduction in the number of the micelles is attended by precipitation. This precipitation is reversible, the precipitate which forms upon dilution disappearing at the same point when the concentration of colloidal electrolyte is increased. The presence of 0.0025 *N* sodium succinate greatly reduces the critical concentration of dodecylammonium chloride. It is significant that the

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[6] Ralston, Hoffman, Hoerr and Selby, THIS JOURNAL, **63**, 1598 (1941).

[7] Ralston, Hoerr and Hoffman, *ibid.*, **63**, 2576 (1941).

[8] Pool, Harwood and Ralston, *ibid.*, **67**, 775 (1945).

critical point in the presence of 0.0025 N succinic acid is identical with that in pure water, thus indicating the removal of the succinic acid from solution as a molecular complex.

A comparison of the effects of tartaric acid and sodium tartrate (Fig. 11) is of interest since precipitation is encountered with as low as 0.0025 N sodium tartrate whereas 0.02 N tartaric acid increases the critical concentration. Such an increase is easily explainable on the basis of complex formation.

A study of Fig. 12 shows that sulfuric acid brings about precipitation at approximately the same concentration as sodium sulfate. This indicates that, under the experimental conditions employed, complex formation between the components does not occur.

Studies of the electrical conductivity of dodecylammonium chloride in water–organic solvent systems[9] show that the addition of a solvent such as methanol or ethanol to aqueous solutions of this colloidal electrolyte greatly increases the concentration at the critical point. This effect is the opposite of that produced by the addition of salts and should be nullified by such additions. Figure 1 shows the electrical conductivity of dodecylammonium chloride in 25 vol. per cent. aqueous methanol, and in 0.02 N sodium chloride in 25 vol. per cent. aqueous methanol as well as in sodium chloride solutions. The critical concentration in the sodium chloride–methanol system is approximately the average of those of the methanol solution and the 0.02 N sodium chloride solution, thus indicating that the effects of sodium chloride and methanol are mutually compensating.

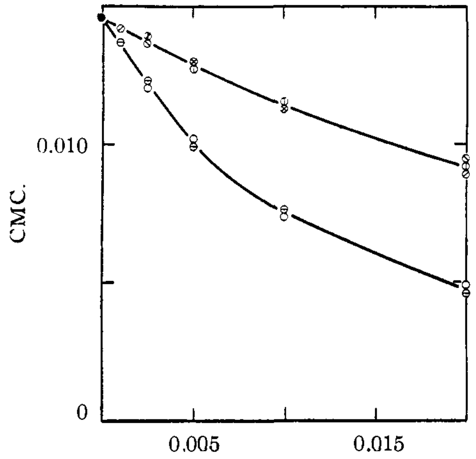

Fig. 13.—Critical concentration of dodecylammonium chloride in presence of chlorides and nitrates at 30°: ○, HNO_3; ⊖, $NaNO_3$; ⦶, HCl; ⦸, $BaCl_2$; ⊘, NaCl.

Summary

The conductivity by difference of dodecylammonium chloride has been determined in the presence of a number of salts and acids.

Salts and strong acids reduce both the equivalent conductivity and the critical concentration. The reduction of the critical concentration in the presence of such electrolytes is independent of the nature and concentration of the cation of the added electrolyte. Weak acids, on the other hand, form molecular complexes with dodecylammonium salts and their presence does not reduce the critical concentration.

The addition of sodium succinate, sodium tartrate or sodium sulfate brings about precipitation in dilute aqueous solutions of dodecylammonium chloride. This effect is not encountered with weak acids owing to molecular-complex formation.

The increase in the critical concentration of dodecylammonium chloride brought about by the addition of methanol is nullified by the addition of sodium chloride.

CHICAGO, ILLINOIS RECEIVED NOVEMBER 10, 1948

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[9] Ralston and Eggenberger, *J. Phys. and Colloid Chem.*, **52**, 1494 (1948).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Metal–Salt Interactions at High Temperatures: The Solubilities of Some Alkaline Earth Metals in their Halides[1]

BY D. D. CUBICCIOTTI[2] AND C. D. THURMOND

It has long been known that certain metals may be dispersed in their molten salts.[3] The phases thus formed, when chilled to room temperature, are salt-like, intensely colored, good reducing agents (of the order of the metal dispersed in them) and may have globules of metal embedded in them. This phenomenon was attributed to the reduction of the salt by the metal at high temperature with the formation of a lower valent salt (unstable with respect to the metal and normal salt at room temperature). Later work, due mainly to R. Lorenz,[4] attempted to show that the metal was being colloidally dispersed throughout the salt. In the case of bismuth and

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[1] This research was directed by the late Prof. E. D. Eastman and carried on for the Manhattan Project.

[2] Present address: Department of Chemistry, Illinois Institute of Technology, Chicago, Ill.

[3] Davy, *Trans. Roy. Soc.* (*London*), **97**, 1 (1807); Bunsen and Kirchhoff, *Pogg. Ann.*, **113**, 364 (1861); Stockem, *Z. angew. Chem.*, **17**, 341 (1904); Guntz and Benoit, *Bull. soc. chim.*, [4] **35**, 709 (1924).

[4] Lorenz and Eitel, "Pyrosole," Leipzig, 1926.