ture of the complexes of zinc chloride and zinc nitrate with N,N′-diacetylethylenediamine.

Experimental[3]

N,N′-Diacetylethylenediamine Nitrate.—N,N′-Diacetylethylenediamine was prepared by adding 63 cc. (0.66 mole) of acetic anhydride dropwise to 18 g. (0.3 mole) of anhydrous ethylenediamine. To the warm mixture was added 168 cc. (1.8 mole) of acetic anhydride, and this solution (kept homogeneous by warming) was added during eighty minutes to 75 cc. (1.8 mole) of 100% nitric acid which was stirred at 0–5°. After addition was complete the mixture was stirred for two hours at 0–5°. The solid present in the reaction mixture was collected on a sintered glass funnel and washed with acetic acid and ether. The precipitate was stirred with 200 cc. of water. The insoluble material (N,N′-diacetyl-N,N′-dinitroethylenediamine), which was removed by filtration, weighed 11.6 g. and melted at 127.7°. By concentration of the aqueous filtrate to dryness *in vacuo* (bath temperature 50–60°, higher temperatures cause decomposition) there was obtained a residue of white crystalline N,N′-diacetylethylenediamine nitrate weighing 29.5 g. After several recrystallizations from butanone, this substance melted constantly at 120.7–122.6°. It crystallizes in clusters of short heavy needles.

Anal. Calcd. for $C_6H_{13}O_5N_3$: C, 34.78; H, 6.33; NO_3, 29.92. Found: C, 35.05, 34.99; H, 6.57, 6.63; NO_3 (by titration), 29.80.

This nitrate is not hygroscopic, but on standing it decomposes within a few days, as evidenced by a dropping of the m. p.

This salt was also prepared by evaporating to dryness *in vacuo* a mixture of 50 g. of N,N′-diacetylethylenediamine, 75 cc. of water and exactly one equivalent of standardized concentrated nitric acid. The yield of nitrate was 68.8 g. (96%), m. p. 112.5–122.3°. After one crystallization from butanone, this material melted at 120.1–122.6° and gave no depression of m. p. on mixing with the sample isolated from the nitration reaction.

The complex of N,N′-diacetylethylenediamine and zinc chloride was obtained in quantitative yield by mixing equimolar amounts of zinc chloride and N,N′-diacetylethylenediamine in butanone or in acetic anhydride. It is non-hygroscopic and, after crystallization from glacial acetic acid, melts at 185.8–186.6°. The melting point of its mixture with the hygroscopic complex described below is depressed to 164–173.5°.

Anal. Calcd. for $C_6H_{12}O_2N_2 \cdot ZnCl_2$: C, 25.69; H, 4.31; $ZnCl_2$, 48.59. Found: C, 26.18; H, 4.27; $ZnCl_2$ (by titration of Zn), 48.47.

The hygroscopic complex obtained when N,N′-diacetylethylenediamine nitrate was warmed in acetic anhydride with zinc chloride, crystallized from butanone–alcohol as heavy prisms. Samples recrystallized until the melting point became constant at 187–189° (varying with rate of heating) were analyzed, and the values were C, 27.88; H, 4.72; Zn (by titration), 16.86, 17.02, 16.75; Cl, 7.89, 8.08; NO_3 (with nitron), 18.70, 18.73. The zinc is equivalent to the sum of nitrate and chloride, and the organic portion of the substance, by difference, amounts to 56.4%. This was shown to be N,N′-diacetylethylenediamine by cleavage of the complex with sodium hydroxide and isolation of a quantity of the amide amounting to 54% of the complex. The amide was identified by analysis and by a mixed m. p. with an authentic sample. A complex containing one molecule of amide and one molecule of the mixed salt, $ClZnNO_3$, would contain about 47% amide, and if the ratio of amide to mixed salt were 2:1 the amide content would be about 63%. No other simple combination of amide, zinc, chloride and nitrate gives values in agreement with the values found.

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[3] All melting points are corrected.

Preparation of Cacodyl Chloride

BY BENJAMIN WITTEN

Bunsen[1] prepared cacodyl chloride by treating Cadet's liquid, which is composed chiefly of a mixture of cacodyl and cacodyl oxide,[2] with mercuric chloride and hydrochloric acid. Steinkopf and Mieg[3] prepared cacodyl chloride by reduction of cacodylic acid with hypophosphite in the presence of concentrated hydrochloric acid. They report the boiling point as 106.5–107°. Skinner and Sutton,[4] who prepared cacodyl chloride by this method, report the boiling point as 106–107°. Valeur and Gailliot[5] prepared it by reduction of cacodylic acid with stannous chloride and hydrochloric acid, and list the boiling point as 107°. Lee, Thing and Dehn,[6] who prepared it by Bunsen's method, list the boiling point as 109°.

The advantage of the method of Steinkopf and Mieg or of Valeur and Gailliot, over Bunsen's method is that it eliminates the handling of spontaneously inflammable Cadet's liquid. The method, however, requires oxidation of Cadet's liquid to cacodylic acid and subsequent reduction to cacodyl chloride.

In this paper, there is reported a procedure for preparing cacodyl chloride from potassium acetate and arsenic trioxide without the necessity of isolating the spontaneously inflammable Cadet's liquid, as is required by Bunsen's method, and without the necessity of oxidation to cacodylic acid and subsequent reduction to cacodyl chloride, as is required by the method of Steinkopf and Mieg or of Valeur and Gailliot. It was found that ferric chloride could be substituted for the mercuric chloride used by Bunsen.

Experimental

Cacodyl Chloride.—Into a 2-quart cast-iron retort was placed a mixture of 750 g. of potassium acetate and 750 g. of arsenic trioxide. The retort was connected to a condenser, and then to a receiver consisting of a 2-liter balloon flask into which was introduced a solution of 1000 g. of hydrated ferric chloride dissolved in 500 ml. of concentrated hydrochloric acid. The receiver was cooled in an ice-bath during the run. The distillation was carried out on a sand-bath. Distillation began at a bath temperature of about 300° and was complete after six hours, at which time the bath temperature reached 350–400°. Cadet's liquid which formed during the distillation reacted with the ferric chloride and hydrochloric acid in the receiver to form cacodyl chloride. The resulting ferric chloride mixture in the receiver consisted of a lower brownish-green paste and an upper red liquid layer. After the distillation, the receiver was disconnected from the system, was stoppered, and was allowed to stand overnight.

The residue in the iron pot was disposed of by dissolving it in water which was added slowly to the retort while it was still hot. If the retort were allowed to cool before removing the residue, difficulty was encountered in removing the solid cake which formed.

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(1) Bunsen, *Ann.*, **37**, 1 (1841); Baeyer, *ibid.*, **107**, 257 (1858).

(2) Dehn and Wilcox, *Am. Chem. J.*, **35**, 1 (1906).

(3) Steinkopf and Mieg, *Ber.*, **53**, 1016 (1920); Augur, *Compt. rend.*, **142**, 1152 (1906).

(4) Skinner and Sutton, *Trans. Faraday Soc.*, **40**, 164 (1944).

(5) Valeur and Gailliot, *Bull. Soc. Chim.*, **41**, 1485 (1927).

(6) Dehn, THIS JOURNAL, **45**, 2993 (1923).

The mixture in the receiver was distilled at atmospheric pressure in an atmosphere of carbon dioxide. Two layers formed in the distillate—a lower cacodyl chloride layer and an upper aqueous layer. The lower cacodyl chloride layer was separated, washed with 100 ml. of water and dried over 20 g. of calcium chloride. There was obtained 150 g. of product (28% of theoretical based on potassium acetate), which had a boiling point of 106–109° at atmospheric pressure.

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The Skraup Reaction with Acrolein and its Derivatives. I. The Preparation of 6-Methoxy-8-nitroquinoline

BY HARRY L. YALE

The role of acrolein as an intermediate in the Skraup reaction has been accepted generally. The poor yield of quinoline from the product of the reaction between aniline and acrolein has been considered, however, as indirect evidence for another mechanism.[1] The Doebner–Miller modification of the Skraup reaction, which employs β-substituted acrolein derivatives, has been used with success in the preparation of 2-substituted quinolines and this has given additional weight to the probability that acrolein does exist, at least momentarily, during the Skraup reaction. Recently, Manske[2] has employed α-methylacrolein and its dimethyl acetal and Utermohlen[3] has used α-methylacrolein, α-ethylacrolein, their diacetates and dipropionates, to prepare a number of 3-substituted quinoline compounds. Quinoline compounds with alkyl substituents in the 4-position have been prepared by the reaction of alkyl vinyl ketones with aniline. In 1907, Blaise and Maire[4] reported that the condensation product of ethyl vinyl ketone and aniline gave 4-ethylquinoline on heating with aniline hydrochloride. Later, Prill and Walter[5] found that 4-substituted quinolines could be prepared in good yield by the reaction between methyl vinyl ketone, its homologs and derivatives, and an aromatic amine in the presence of sulfuric acid and an oxidizing agent such as nitrobenzene or arsenic acid. Recently Campbell and his associates[6] have further developed this modification of the Skraup reaction to prepare a number of lepidines.

Our interest in preparing 6-methoxy-8-nitroquinoline caused us to investigate the same reaction, employing acrolein in place of methyl vinyl ketone under somewhat milder conditions. We wish to report at this time that the desired quinoline derivative was obtained in 42.3% yield. Since aniline and acrolein under these conditions gave no more than traces of quinoline, it appears likely that some activation of the *ortho* hydrogen is necessary for ring closure.

Work is now in progress in these laboratories on the further development of this reaction.

Experimental

All melting points are uncorrected.

Preparation of 6-Methoxy-8-nitroquinoline.—An intimate mixture of 168 g. (1.0 mole) of 3-nitro-4-aminoanisole, 132 g. of arsenic pentoxide, 152 ml. of concentrated sulfuric acid and 72 ml. of water was heated to 80°. To this was added dropwise 70 ml. of acrolein during two hours, maintaining the temperature at 75–80°. After the addition of the acrolein, the mixture was heated to 120° during one hour, cooled, diluted to five liters with water and filtered. The filtrate was neutralized with ammonia and the precipitated 6-methoxy-8-nitroquinoline was collected on a filter and air dried. After purification it melted at 157° and a mixed melting point with an authentic sample of 6-methoxy-8-nitroquinoline, prepared by the Skraup reaction, was 157°. The yield was 86.5 g. or 42.3% of the theoretical amount.

Reaction between Aniline and Acrolein.—The reaction was carried out as above except that 93 g. (1.0 mole) of aniline was substituted for the 3-nitro-4-aminoanisole. Subsequent to heating the reaction mixture to 120°, it was diluted with water and made alkaline with 40% sodium hydroxide solution. A large amount of semi-solid black material separated. The mixture was steam distilled to isolate any quinoline as well as the unreacted aniline. The steam distillate was extracted with ether, the ether extracts were dried and the ether removed by distillation. The entire residual oil distilled at 79–82° (20 mm.), weighed 12.0 g. and was identified as aniline by conversion to the *p*-toluenesulfonanilide, m. p. 109–110°. The reported melting point of this compound is 112°.

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(1) Bergstrom, *Chem. Rev.*, **35**, 77 (1944); Manske, *ibid.*, **30**, 113 (1942).

(2) Manske, Marion and Leger, *Can. J. Research*, **B20**, 133 (1942).

(3) Utermohlen, *J. Org. Chem.*, **8**, 544 (1943).

(4) Blaise and Maire, *Compt. rend.*, **144**, 93 (1907); *Bull. soc. chim.*, [4] **3**, 667 (1908).

(5) Prill and Walter, U. S. Patent 1,806,563 and 1,806,564; *C. A.*, **25**, 3668 (1931).

(6) Campbell, *et al.*, THIS JOURNAL, **67**, 86 (1945); **68**, 1837 (1946); abstracts of the American Chemical Society, Chicago meeting, Sept. 9–13, 1946.

NEW COMPOUNDS

Methylammonium Sulfamate

Ten grams of sulfamic acid was dissolved in water and neutralized with aqueous methylamine. The water was removed under reduced pressure on a steam-bath and the warm liquid residue (quantitative yield) was crystallized from methyl alcohol and dried *in vacuo* at 75°. The dense white needles melted at 91–93° and were found to be deliquescent.

Anal. Calcd. for $CH_8O_3SN_2$: N, 21.87. Found: N, 21.9.

Solubility in 100 g. of boiling solvent: methyl alcohol, over 124 g.; 2-B anhydrous ethyl alcohol, 2.3 g. From ethyl alcohol it separates in thin clear plates, m.p. 91–93°.

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KANSAS CITY, MISSOURI LOUIS H. GOODSON
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Some Esters of 2-Furoic Acid

The new compounds listed in Table I were prepared through the acid chloride.