

tial" and "current efficiency," in the case of closely related aldehydes and ketones, lie too close together to permit of the method of electrolytic reduction being used to distinguish between the small differences represented by their "residual valences." Further refinements in the measurement of both factors appear of little use in view of the limitations imposed by the non-reproducibility of the cathode.

5. It is thus improbable that such values are likely to be of much assistance in determining the "relative, residual valence" of carbohydrates, anhydro-sugars and polysaccharides. The relationship of this factor to "tendency towards polymerization" will thus have to be decided by the measurement of other properties more sensitive to slight changes in structure.

6. Crotonaldehyde on reduction gives as principal product, a new derivative, dimethylcyclopentene aldehyde.

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[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF WASHINGTON]

THE LABORATORY PREPARATION OF DIETHYL SULFATE

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After a careful experimental check of the methods which have been proposed, we have arrived at the conclusion that no satisfactory one has yet been presented for the preparation of diethyl sulfate. Since this substance has recently achieved prominence as an ethylating agent¹ of considerable value, a convenient method of manufacture on a laboratory scale would undoubtedly be of great service to many of those pursuing research work with organic substances. Of the several general processes given in the literature,² we may reasonably reject most as unsuitable to laboratory practice, unless other methods should not prove efficient.

¹ Cade, *Chem. Met. Eng.*, **29**, 319 (1923).

² Wetherill, *Ann.*, **66**, 117 (1848). Baumstark, *ibid.*, **140**, 78 (1866). Claesson, *J. prakt. Chem.*, [2] **19**, 255 (1879). Mazurowska, *ibid.*, [2] **13**, 158 (1876). Orłowsky, *Ber.*, **8**, 332 (1875). Stempnewsky, *ibid.*, **11**, 514 (1878). Claesson and Lundvall, *ibid.*, **13**, 1699 (1880). Villiers, *Compt. rend.*, **90**, 1291 (1880). Damiens, *ibid.*, **175**, 585 (1923). Curme, G. O. and H. R., *Chem. Met. Eng.*, **25**, 957 (1922). Lilienfeld, U. S. pat. 1,074,633 [*C. A.*, **7**, 4046 (1913)]; Ger. pat. 272,339 [*C. A.*, **8**, 3100 (1914)]; Brit. pat. 143,260 [*C. A.*, **14**, 2802 (1920)]; U. S. pat. 1,427,215 [*C. A.*, **16**, 3665 (1922)]. Merck, Ger. pat. 133,542 (1902). Leproux, Fr. pat. 421, 628 [*C. A.*, **6**, 1981 (1912)]. Wolf, U. S. pat. 1,101,373 [*C. A.*, **8**, 2922 (1914)]; Aus. pat. 8,495, 9,624 [*C. A.*, **9**, 513 (1915)]. Curme, U. S. pat. 1,339,947 [*C. A.*, **14**, 2001 (1920)]. Kuh, Brit. pat. 149,688 [*C. A.*, **15**, 374 (1921)]; U. S. pat. 1,411,215 [*C. A.*, **16**, 1781 (1922)]. Sidgwick and Plant, Brit. pat. 157,578 [*C. A.*, **15**, 1905 (1921)]. Bader, Brit. pat. 175,077 [*C. A.*, **16**, 2149 (1922)]. Engelhardt, Lommel and Ossenbeck, U. S. pat. 1,458,646 [*C. A.*, **17**, 2587 (1923)]. Dreyfus, Brit. pat. 177,189 [*C. A.*, **16**, 3094 (1922)].

The production of diethyl sulfate from ethylene can be efficiently carried out on a commercial scale, where this process can be made continuous. In the laboratory, however, ethylene is not ordinarily available and must be made by the dehydration of alcohol. The amount of diethyl sulfate is very small and the amount of time required is prohibitive even if an apparatus is used which gives maximum absorption efficiency.

Ethyl hydrogen sulfate is formed when alcohol and sulfuric acid are mixed, and Evans and Albertson³ in their study of the formation of ethyl sulfuric acid suggest the possible formation of diethyl sulfate on allowing the mixture to stand for some time. Since the diethyl sulfate decomposes at the higher temperatures and even at low temperatures by continued boiling, the distillation of large volumes of mixtures, which may form this compound, probably gives a low yield because it is decomposed by the long continued heating necessary during the process of distillation. Heating under a reflux condenser with a dehydrating agent and then distilling in a vacuum did not give a satisfactory yield. It was then decided to arrange the process in such a manner as to remove the diethyl sulfate as soon as it was formed by allowing only a small portion of the mixture at a time to come in contact with the dehydrating agent. After a number of experiments, we decided that the following method would give the best results. Ninety g. of anhydrous sodium sulfate is placed in a dry 1-liter flask connected with a condenser and receiver arranged for vacuum distillation. The flask is heated by means of an oil-bath kept at a temperature of 155–165°. The apparatus is exhausted as nearly as possible by means of a filter pump, and a mixture of 50 g. of alcohol and 104.5 g. of concd. sulfuric acid is allowed to drop through a capillary tube upon the sodium sulfate at a rate of about 120–150 drops per minute. The distillation of this mixture requires about one and one-half hours for completion. The distillate, which consists of alcohol and diethyl sulfate in two layers, is separated by means of a funnel. The alcohol thus recovered may be used in subsequent operations. The diethyl sulfate is washed with a dilute solution of sodium carbonate and then several times with cold water, dried over anhydrous sodium sulfate and filtered. The product thus obtained is neutral to litmus and analysis proves it to be almost pure diethyl sulfate; yield, 32.6 g.

The temperature as given above is the optimum for the largest yield of diethyl sulfate, as is shown by the following experiments. The pressure was 20 to 45 mm.

Temp. of bath, °C.	130–140	140–150	150–160	160–170	170–180	190–200
Yield, g.	8	19.9	32.6	32.5	25.7	20.8

Other dehydrating agents such as sodium pyrosulfate or anhydrous magnesium sulfate were used but the yield was lower in each case. In-

³ Evans and Albertson, *THIS JOURNAL*, 39, 456 (1917).

creasing or decreasing the amount of sulfuric acid causes a lower yield. Absolute alcohol does not have any advantage over 95% alcohol nor does fuming sulfuric acid have any advantage over the ordinary concentrated acid.

The analysis of the crude diethyl sulfate was carried out as follows.

A 2 to 3 g. sample of diethyl sulfate, accurately weighed, is placed into a 250cc. Erlenmeyer flask, and 5 g. of barium hydroxide and 100 cc. of water are added. The mixture is heated just below the boiling point for three hours. It is allowed to cool and the excess of barium hydroxide removed by filtration. The filtrate is saturated with carbon dioxide, filtered and the residue thoroughly washed with distilled water. Sulfuric acid is then added to the filtrate until the barium is completely precipitated as barium sulfate. The mixture is then heated to boiling and filtered and the precipitate is washed, dried and weighed.

In two such analyses 51.03 and 51.27% of sulfur trioxide equivalent were found, as compared with the calculated value, 51.94.

Summary

A convenient process for the laboratory preparation of diethyl sulfate is given, together with a method for the analysis of this compound.

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A MODIFICATION OF THE SANDMEYER SYNTHESIS OF NITRILES

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The convenient method devised by Sandmeyer¹ for the replacement of aromatic amino groups by the nitrile radical involves the formation of a solution of potassium cuprocyanide by the addition of cupric sulfate to potassium cyanide, and the addition of an acid solution of a diazonium salt to the resulting mixture. During the reduction of the cupric salt to the cuprous condition cyanogen is liberated, while hydrogen cyanide is evolved on adding the acid solution to the cuprocyanide mixture. Modifications of the original process have been suggested² but apparently no attempt has ever been made to avoid the evolution of poisonous gases.

We have found that a solution of sodium cuprocyanide can be very satisfactorily prepared by dissolving cuprous chloride in sodium cyanide solution; when the diazonium solution is neutralized under suitable conditions, its reactivity is, in all cases which we have examined, unimpaired. When a solution of benzenediazonium chloride, which has previously been neutralized at 0-4°, is poured into a cold solution of sodium cupro-

¹ Sandmeyer, *Ber.*, **17**, 2653 (1884); **18**, 1492, 1496 (1885).

² *Ber.*, **19**, 756 (1886); **23**, 1026 (1890).