

ADDITION PRODUCTS OF ANILS WITH METALLIC CHLORIDES

IN course of some synthetic work for the preparation of ethyl acetoacetate-anil, ethyl acetoacetate was reacted with aniline in presence of fused zinc chloride. On working up the reaction product a well-defined crystalline compound was obtained which melted above 240° C. over a wide range and with decomposition. The same product was obtained from ethyl acetoacetate-anil and zinc chloride and was found to be the addition product of the anil and zinc chloride, $C_{15}H_{15}O_2N$, $ZnCl_2$, as on decomposition with sodium carbonate it gave the anil which by Conrad and Limpach's method¹ could be converted to 4-hydroxy-2-methylquinoline. Similar addition products were also obtained from the anil and cadmium and mercuric chlorides. No such addition product of anils appears to be known in literature.

Ethyl α -methylacetoacetate-anil gave similar addition products with zinc and mercuric chlorides. Anils from *o*-anisidine and *o*- and *p*-toluidines and ethyl acetoacetate also gave addition products with zinc and cadmium chlorides. Acetophenone-anil and benzaldehyde-anil however, failed to give any addition product with zinc chloride and got hydrolysed yielding aniline-zinc chloride. Hence the formation of addition products with the above metallic halides appears to be the property of anils of β -ketonic esters only, and would be useful for isolation of anils from an impure mixture and for their characterisation.

Detailed account of the work will be published elsewhere.

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1. Conrad and Limpach, *Ber.*, 1887, 20, 947; Limpach, *Ber.*, 1931, 64, 969; Hughes and Louis, *J. Proc. Roy. Soc., N. S. Wales*, 1938, 71, 458; Cavallito and Haskell, *J. Am. Chem. Soc.*, 1944, 66, 1166.

AMESITE FROM DEVARNARSIPUR, BHADRAVATHI, MYSORE

In a petrographic collection made by Dr. C. S. Pichamuthu from Devarnarsipur, in the year

	Devarnarsipur	Pisani	Shannon
SiO ₂	28.60	21.40	20.95
Al ₂ O ₃	31.02	32.30	35.21
Fe ₂ O ₃	Nil	Nil	Nil
FeO	4.80	15.80	8.28
MgO	23.44	19.90	22.88
CaO	Nil		0.58
MnO	0.37	..	traces
H ₂ O+	11.90	10.90	13.02
H ₂ O-	0.27		0.23
	100.40	100.30	101.15

1943, occurs an interesting type of rock, which at first sight appears to be an amphibolite. But, on closer examination, it is found to be a chlorite-tourmaline rock. As the chlorite found in this rock appears to be particularly interesting, this mineral has been subjected to a detailed investigation of its optical characters and chemical composition and the main conclusions are recorded below. The chlorite is amesite and the tourmaline is schorlite. The analysis of the amesite¹ is given here and is compared with two others described by Shannon and Pisani.²

The optical characters of the amesite as compared with that, described by Shannon, from Chester, are as follows:—

Devarnarsipur	Chester ³
(+) 2V = 0° to 15° 45'	(+) 2V = 0°
Ng = 1.590	Ng = 1.612
Nm = 1.585	Nm = N _p = 1.597
N _p = 1.575	N _g - N _p = .015
N _g - N _p = .015	
Pleochroic	Colourless

The Mysore amesite differs from that of Chester in being pleochroic, X=Y= pale green, Z= colourless and showing a character varying from uniaxial to biaxial, with a maximum optic axial angle 2E=26° (calculated to 2V=15° 45'), measured on the Federvo's stage. The silica percentage of the Mysore amesite is higher than that given by Shannon and Pisani. Pisani's formula for amesite, which has been adopted by Winchell, is $H_4Mg_3Al_2SiO_9$.⁴ Since silica is known to replace alumina in the structure of these minerals, Pisani's formula for amesite may be modified for Mysore amesite as $H_4(Mg, Fe, Mn)_3(Si, Al)_3O_9$.

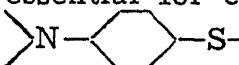
Plotted on the linear diagram proposed by Hammond⁵ for chlorite minerals, the Mysore amesite has RO: SiO₂ = 296 and R₂O₃: SiO₂ = 127, and lies in the amesite field.

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1. Analyst—E. R. Tirumalachar, Chemist, Mysore Geological Department. 2. *American Journal of Science*, 1920, 49, 96. 3. *Op. cit.* 2 above. 4. *American Mineralogist*, 1936, 21, 642. 5. *The Mineralogical Magazine*, 25, No. 167, 454.

SCHIFF'S BASES OF 4-4'-DIAMINODIPHENYLSULPHIDE



THE high antibacterial activity of 4-4'-diaminodiphenyl sulphone and sulphanilamides has led to the belief that the molecular grouping essential for chemotherapeutic activity is the

 N—C₆H₄—S—Complex.^{1,2} Raiziss, *et al.*³ reported that, although the therapeutic properties of 4-4'-diaminodiphenylsulphide and its acetyl derivative compared favourably with those of sulphanilamide, their high toxicity

precluded their clinical use. The Schiff's bases of sulphanilamides and N'-substituted sulphanilamides have all been found to be very effective against bacterial infections.⁴

Considering the above facts it was thought worthwhile to synthesise a few typical Schiff's bases (Type A) of 4-4'-diaminodiphenyl sulphide for testing their antibacterial activity. The Schiff's bases (Table I) have been prepared by reacting 4-4'-diaminodiphenyl sulphide with appropriate aldehydes in alcoholic solution and in the presence of condensing agents like zinc chloride. The resulting compounds have been crystallised from alcohol. They have been characterised and listed in Table I.

TABLE I

General formula Type A. $R'CH=N-$  $-S-$
 $-N=CH \cdot R$. R = aldehyde residue.

No.	Aldehyde used	M.P. ° C.
1	Benzaldehyde	176-177
2	m-Nitrobenzaldehyde	159-160
3	p-Dimethylamino benzaldehyde	231-232
4	p-Diethylamino benzaldehyde	155-156
5	Salicylaldehyde	207-208
6	Anisaldehyde	204-205
7	Piperonal	175-176
8	Cinnamaldehyde	178-179
9	Furfural	103-104

Details will be published elsewhere.

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OXIDATION OF CYSTINE BY NITRIC ACID

BLUMENTHAL AND CLARKE¹ found that nitric acid oxidises cystine sulphur to sulphuric acid. Evans² adopted this method for the estimation of cystine in food materials by conversion to sulphate and estimating the latter as barium sulphate. He, however, observed that with pure cystine only about 62% of the cystine could be recovered as sulphate. Addition of

dextrose, soya-bean meal or fish meal along with the cystine increased the recovery to 92-98%. The following note relates to some observations made on the above reaction.

It was first observed that however long the reaction mixture of cystine and nitric acid be heated on the water-bath, the percentage recovery of cystine as sulphate was incomplete. It varied from 62.1% to 66.3%. If after heating the reaction mixture for 24 hours as suggested by Evans, dextrose be added to the reaction mixture and it is further heated for 6-8 hours, 93.6% of the cystine sulphur could be oxidised to sulphate. This experiment showed that incomplete recovery of cystine as sulphate was due to incomplete oxidation and not due to loss of cystine sulphur as oxides of sulphur during the oxidation with nitric acid.

The following table shows the effect of addition of various substances to the cystine prior to oxidation on the conversion of cystine sulphur to sulphate sulphur.

From the results (see table) it can be postulated that during the oxidation of the (-S-S-) linkage of cystine by nitric acid about 1/3 of the cystine is converted to one or more intermediate oxidation products which resist complete oxidation to sulphate by nitric acid alone. Any type of organic matter which can reduce nitric acid to lower oxides of nitrogen if added to the reaction mixture in the beginning of the reaction or at any later stage of the reaction, can catalyse the complete oxidation of these intermediate products to the sulphate stage. The fact that even inorganic substances like copper, zinc or tin which reduce nitric acid to oxides of nitrogen are capable of acting in a way similar to organic materials has to be interpreted to mean that the further oxidation of the intermediate products is brought about by the intervention of the oxides of nitrogen. Further examination of the filtrate from the Barium sulphate precipitation mixture would reveal the nature of the intermediate oxidation products.

The author's thanks are due to Dr. V. Subrahmanyam and Dr. M. R. Aswathanarayana Rao for their interest in the work.

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Note.—0.1 g. samples of cystine were taken for each estimation 2g of lactose, glucose starch, and butter fat were added along with the cystine during the digestion. The amounts of carbon, zinc, copper, and tin added along with the cystine were 1.5 g. in each case.

	Substances added								
	Control	Glucose	Lactose	Starch	Butter fat	Pure carbon	Copper	Tin	Zinc
Cystine recovered as sulphate	63.8%	95.2%	94.5%	95.8%	95.7%	96.9%	95.2%	96.7%	97.1%