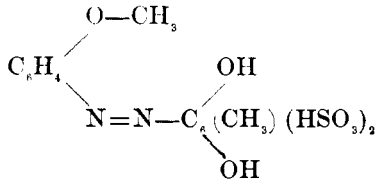
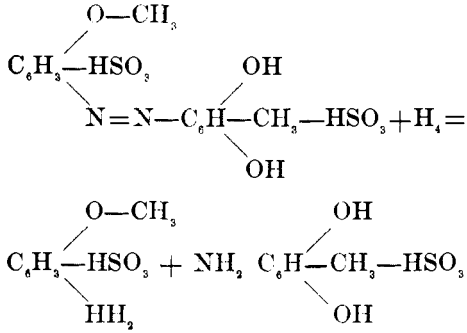
among the two benzole nuclei, instead of their both being contained in the benzole nucleus pertaining to the orcine ; thus :



This would therefore account for the absence of anisidine among the reduction products. As a compound of the foregoing constitution, would probably split up on reduction, into anisidine sulpho-acid, and amido orcine sulpho-acid ; thus :



As both there substances are sulpho-acids, they would probably not be precipitated by caustic soda, but, would combine with the latter to form soda salts.

ACROLEIN-UREA, WITH REMARKS UPON MR. HUGO SCHIFF'S PUBLICATIONS UPON CONDENSED UREAS.

By Albert R. Leeds.

I find that Mr. Hugo Schiff* attributes my statement (this Journal, iv. p. 58) that the body which he described as Acryldiureid.

$$\left.\begin{matrix} CO.N_2H_3 \\ CO.N_2H_3 \end{matrix}\right\} C_3H_4$$

(Ann. Chem. Pharm. 151, 203), is in reality Acrolein-urea, $CO.(NH)_2\ C_3\ H_4$, to the fact that I had not consulted his original

* Ber. dentsch. Chem. Gesell. xv. 1393.

memoir, but an incorrect extract therefrom. I wish to state expressly that this was not the case, and that my own experiments were conducted with constant reference to Mr. Schiff's original memoir in the Ann. Chem. Pharm. loc. cit., and that I did not isolate the compound containing the residue from 2 molecules of urea, but only the compound with the residue from one molecule or CO. $(NH)_2$ C_3 H_4. Furthermore, I wish to state that the non-crystalline, white body which I obtained by the purification of the precipitate which ensues when acrolein is added to an alcoholic solution of urea, and found to be CO. $(NH)_2$ C_3 H_4, is the same compound as is obtained when an aqueous solution of urea is treated with acrolein, in the manner described by Mr. Schiff, but which he did not purify adequately, and to which he consequently gave the erroneous formula of an Acryldiureid.

In his criticism upon my article, Mr. Schiff says that he analyzed this compound which he obtained with an aqueous solution of urea, and that it contained 38.3 per cent. carbon, the right percentage for Acryldiureid. But in the memoir to which Mr. Schiff has referred me no such analysis is given, and if this analysis is not contained in that memoir, I desire to be referred to some article published before this reply of Mr. Schiff, in which it can be found.

I have stated that I was able to isolate, and that with much difficulty, but one compound in a state of purity, and for that reason I analyzed only this one compound, finding in it Carbon 49.01 per cent. (accidentally misprinted in the Berichte 40.01 per cent.) and Hydrogen 6.30 per cent. There is undoubtedly a resinous, oily by-product, to whose presence the difficulty of obtaining the pure compound is due. But Mr. Schiff has analyzed the various mixtures obtained after more or less partial purification, and deemed that he was entitled on the strength of such analyses so conclude in the first place that he had *isolated* Acryldiureid, and that another body, which he did not isolate but obtained as a white porcelain-like substance intimately mixed with acrolein was Diacryltriureid, 42.2 per cent. Carbon and 6.3 per cent. Hydrogen. The figures which he obtained by analysis of this mixture, and which are the only figures given in the memoir he has referred me to, varied between C. 44–47 per cent. and H. 6.9–7.1 per cent.

The method which Mr. Schiff employed to obtain his Diacryltriureid, by treating pulverized urea directly with acrolein, no solvents being employed, was one which required more than usual care and perseverance in the consequent treatment of the product with

solvents in order to separate the bodies thus formed in a state of purity. No such precautions are stated to have been used. On the contrary in his reply to my article, Mr. Schiff has persisted in his plan of making analyses of mixtures, and from his results, he has inferred the presence in these mixtures of no less than three compounds, the composition of anyone of which differs widely from the figures actually obtained.

I think the majority of chemists would find it difficult to believe that Mr. Schiff has endeavored to support the erroneous conclusions arrived at in his original memoir in the Ann. Chem. Pharm., by methods even more inexact and reprehensible, were they not to read his own statements contained in the Berichte XV, 1395. He states there that a portion of the product obtained by the direct action of Acrolein upon Urea, after keeping for 14 years, had undergone a peculiar alteration. About two-thirds had become of a strong canary color, "und man sieht deutlich, wie die Stücken von einer weissen Masse durchzogen sind, so dass die gelben Stücken ofters centrale weisse Stellen zeigen und hierdurch oxalartiag und fast perlmuttuähnlich aussehen. Die Antheile von Krystallinische Aussehen haben dieses Aussehen sowie ihre weisse Farbe bewahrt, aber man Kann jetzt auch bei diesen Stückchen, bei Vergrosserung, um so besser sehen, dass noch gelbe und porcellanartig weisse Substanz innigst beigemengt ist. Leider war gerade diese letztere, weniger cohärente Masse grössten theils zu grobern Pulver zerfallen."

And yet the constituents of a mixture like this, which it would have required great care to have properly separated by means of appropriate solvents, Mr. Schiff attempted to separate by mechanical means, and to pick them out by the aid of a magnifier.

He thus obtained (1) "Gelbe amorphe Substanz mit wenig wiesser porcellanartiger Substanz durchzogen," and with the composition C. 46.81 p ct., H. 7.09 p ct; (2) "Weisse, auscheineud Krystallinische Substanz, noch etwas amorphe weisse und gelbe Verbindung einschliessend," with the composition, C. 45. 15 p ct., H. 6.54 p ct. From these anylyses by a very complicated process of inductive logic, Mr. Schiff concludes that his mixture analyzed consisted of no less than three different compounds, viz :—Acrylureid C. 49 p ct., and H. 6.1 p ct ; Acryldiureid C. 38 p ct., and H. 6.3 p ct., together with Acrylharz C. 60.61 p ct., and H 7–7. 5 p ct.

When we remember that in his original memoir Mr. Schiff stated that the mixture above analyzed contained Diacryltriureid C. 42.2

p ct., and H. 6.3 p ct., and now are told that by a process of logic he infers from analyses performed upon the same material, but much altered after standing 14 years, he has shown that the mixture was really Acrylureid, Acryldiureid and Acrylharz, we are in a position to know how much reliance should be placed either upon the work as first performed, or as afterwards corrected. Mr. Schiff has never isolated Acrylureid, but accepts my own statement as proof of its existence; he has never isolated Acryldiureid, but on the contrary has called Acryldiureid what was in in fact impure Acrylureid, and yet in this final statement he affirms that both these bodies exist in a certain mixture together with an unknown quantity of a resin.

ŒNANTHUREIDE, BENZUREIDE, ŒNANTHO-BENZUREIDE, ETC.

But the foregoing are the smallest among the many marvellous results which Mr. Schiff has arrived at, by applying a great deal of logic to the analyses of complex mixtures. In the original memoir to which he has referred me, he states that he obtained by treating a strong alcoholic solution of Urea with alcohol, Œnanthodiureïd, $C_9 H_{20} N_4 O_2$, (analysis not given) as a crystalline body melting at 166° to a yellow oil. Further on that he obtained by treatment of Œnanthol with crystals of Urea, Diönanthotriureïd, $C_{17} H_{36} N_6 O_3$ (analysis not given), as a crystalline body melting at 162° to a yellow oil. When these two Œnanthureide are treated again with small quanties of Œnanthol, water is formed and the ureide change into "zähe hornige" masses. After cooling these masses are pulverized as far as possible, and extracted with ether. In this manner condensed Ureas are obtained, Trioenanthotetrureid, $C_{25} H_{52} N_8 O_4$ and Pentoenanthohexureid, $C_{41} H_{84} N_{12} O_6$. The former a yellow powder melting about 155°, the latter is a heavy mass which appears to melt at 150°.

When the raw product obtained in the preparation of this hexureid is treated with alcoholic ether and the extract evaporated, there remains behind an amorphous residue. Acetone takes out some œnanthol and leaves a gelatinuous mass which dissolves in alcohol. The solution at a certain degree of condensation solidifies to a glue like substance, which dries to a brittle varnish. This body consists of *twelve* molecules of urea united by the residues from *eleven* molecules of œnanthol, or Dodekoenanathondekaureid:

$$C_{89} H_{180} N_{24} O_{12} = 12\ CH_4 N_2 O + 11\ C_7 H_{14} O - 11\ H_2 O$$

	Calculated.	*Found.*
Carbon	60.1	60.5
Hydrogen	10.1	10.6

But why, according to Schiff's methods of reasoning, should not this glue-like substance solidifying to a varnish be inferred from the analysis to consist of sixteen molecules of urea united with the residues from 15 molecules of œnanthol, this supposition agreeing better with his own results!

$$C_{121}\ H_{244}\ N_{32}\ O_{16} = 16\ C\ H_4\ N_2\ O + 15\ Cy\ H_{14}\ O - 15\ H_2\ O$$

	Calculated.	*Found.*
Carbon	60.5	60.5
Hydrogen	10.2	10.9

It is an extremely fortunate circumstance that, as Mr. Schiff remarks, the ureas more condensed than the hexureid are so very similar in their constitution and so difficult of purification, that he was unable to establish their formulæ "*with certainty.*"

For he truly says, that these substances are very remarkable in regard to their contained nitrogen, since no continuations have ever yet been artificially produced with so large a number of nitrogen atoms. If more of such compounds had been produced the complex nitrogenous substances of animal origin would have appeared simple in comparison.

It is needless to discuss the Benzo-dionanthotetrureid $C_{25}\ H_{44}\ N_8\ O_4$ and the Benzo-tetronanthohexureid $C_{41}\ H_{76}\ N_{12}\ O_6 = 6\ CH_4\ N_2O + 4\ C_7\ H_{14}O + C_7\ H_6 - 5\ H_2O$. Analyses are given which agree sufficiently well with this formula, but they likewise agree with other formulæ which might quite as reasonably be assigned, and it is a dangerous precedent to assign value to analyses of a body stated to be like *dried fibrine* (!) and of whose purity there is no proof whatsoever.

All of the foregoing, and the further work of Mr. H. Schiff upon Anisureïde, Salicylureïde, Æthylsalicylureide, Æthylidenharnstoff, etc., etc., must be repeated, and his results verified, before his views upon the constitution of these condensed ureas can be regarded as worthy of acceptation.