

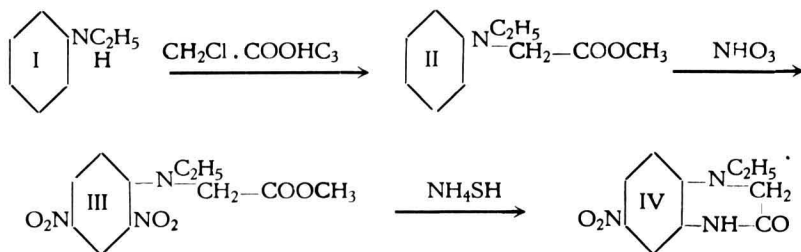
Chemistry. — *Synthesis of 1-ethyl-3-oxo-1:2:3:4-tetrahydroquin-oxaline.* By P. VAN ROMBURGH and W. B. DEYS.

(Communicated at the meeting of September 26, 1931.)

In a communication published some time ago¹⁾ on the action of acetic anhydride and zinc chloride on dinitroderivatives of diethylaniline HUYSER and one of the authors (v. R.) concluded that the products formed by the above mentioned reaction are to be considered as derivatives of tetrahydroquinoxaline and should be represented as nitrated 1-ethyl-3-oxo-1.2.3.4-tetrahydroquinoxaline.

This conclusion was based on their chemical behaviour. It seemed desirable to furnish final proof for the correctness of the proposed formulae.

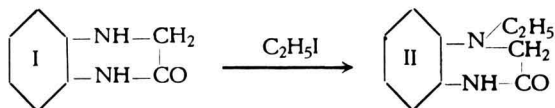
Therefore we have tried in the first place to synthesize the 6-nitro-derivatives of the above mentioned substance by the following reactions:



The result was not favourable because the reduction of III with ammoniumhydrosulfide yielded only an amorphous substance of a dark brown colour from which no definable product could be obtained.

Thereupon we tried the following way, which proved to be more successful.

We prepared 3-oxotetrahydroquinoxaline according to PLÖCHL²⁾ and this substance was ethylated.



If the proposed formulae for the anhydroproducts formed by the reaction of zinc chloride and acetic anhydride on the dinitrodiethylanilines were right, the above mentioned ethylated product might be obtained by reduct-

¹⁾ These Proceedings XXX. 845 (1926).

²⁾ Ber. 19, 8 (1886).

Ethyloxotetrahydroquinoxaline.

I. According to PLÖCHL *o*.nitrophenylaminoacetic acid¹⁾ was prepared and converted by reduction with tin and hydrochloric acid in oxotetrahydroquinoxaline, m.p. 129°. This product (1 mol) was heated with a little more (10 %) than 1 mol of C_2H_5I in a sealed tube at 100° for two hours. The solid content of the tube was dissolved in alcohol, the greater part of the solvent evaporated and the remaining solution taken up in ether. The ethereal solution was shaken with a solution of sodium thiosulfate to remove any traces of free iodine. The residue, after removal of the ether, was dissolved in alcohol. On adding water to this solution an oily product separated, which soon crystallised. On further repeating this procedure a colourless product was obtained m.p. 98—99°, which proved to be the above mentioned substance.

Analysis. Found: C 68.03, 67.97 H 6.78, 6.79
Calculated for $C_{10}H_{12}ON_2$: C 68.18, H 6.81.

II. The reaction product from 2,4 dinitrodiethylaniline with zinc chloride and acetic anhydride was reduced with iron and hydrochloric acid.

The substance was suspended in the hot acid and iron powder added in small quantities. This caused the substance to dissolve. The solution was filtered to remove the excess of iron, evaporated until almost dry and the residue dissolved in alcohol. By passing a stream of hydrogen chloride through the solution white crystals of the hydrochloric salt of the new base deposited. M.p. above 250°.

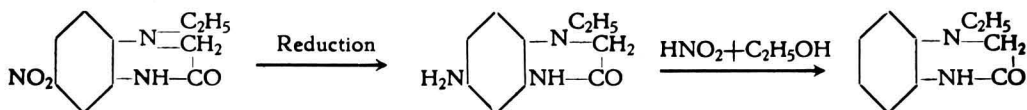
This salt was treated at 0° in alcoholic solution with sulfuric acid and sodium nitrite, and the mixture was heated on a waterbath until the evolution of nitrogen had ceased. After neutralisation a dark product precipitated. This was purified in alcoholic solution by boiling with animal charcoal and further by use of the procedure described above for the purification of ethyloxotetrahydroquinoxaline.

The pure product melted at 96° and did not give a depression of the m.p. when mixed with the synthetically prepared product.

From the identity of these products we conclude that the nitrated anhydroderivatives formed in the reaction of zinc chloride and acetic anhydride on dinitrodiethylaniline possess the structure assigned to them by HUYSER and one of the authors (v. R.).

¹⁾ Attempts to obtain *o*. nitrophenylethylaminoacetic acid by the action of *o*. nitroethyl aniline on bromoacetic acid, even in the presence of pyridine, were unsuccessful.

ion of the anhydro products followed by the substitution of hydrogen for the amino-groups.



The investigation showed that both products were identical.

Experimental.

Methyl ester of phenylethylaminoacetic acid. This ester was prepared by heating a mixture of 1 mol of chloroacetic ester with 2 mol of ethylaniline at 130° . The reaction product after being cooled was poured into water and the separated oily product dissolved in ether. After removing the solvent, the residue was distilled under diminished pressure. An almost colourless oil distilled at $145\text{--}146^\circ$ under 18 mm pressure.

Methyl ester of 2,4 dinitrophenylethylaminoacetic acid.

Two parts of nitric acid (1.4) were slowly dropped into a rapidly stirred, cold (0°) solution of one part of the above mentioned ester in three parts of acetic acid. After the total quantity of the nitric acid had been added, the mixture was allowed to stand for half an hour and then poured into water. A dark coloured crystalline product separated. This was recrystallised from alcohol, and formed yellow crystals melting at 119° which proved to be a dinitroderivative of the ester.

Analysis. Found: C 47.05, 47.11 H 4.61, 4.67 N 14.54, 14.68

Calculated for $\text{C}_{11}\text{H}_{13}\text{N}_3\text{O}_6$: C 46.64 H 4.59 N 14.84

In order to determine the position of the nitrogroups, this product was oxydised with chromic anhydride.

1 g dissolved in 5 cc of boiling acetic acid were treated with 5 cc of a 25 % solution of CrO_3 in acetic acid and water (1:1). After the reaction was over, water was added and a yellow product separated. It was filtered off and recrystallised from alcohol. The product formed in this reaction proved to be 2,4 dinitroaniline. It melts at 180° and did not show a depression of the m.p. when mixed with an authentic sample of 2,4 dinitroaniline.

Analysis. Found: N 22.93

Calculated for $\text{C}_6\text{H}_5\text{N}_3\text{O}_4$: N 22.95

In order to reduce the nitrogroup in position 2 the nitrated ester was treated with ammonium hydrogen sulfide at 50° . The product formed in the reaction was a dark brown mass from which no crystalline product could be obtained.