Victor Auger, Bull Soc Chim 1900, v. 23 pp 333-336

On a new method for preparing nitroalkanes; by V. AUGER.

When potassium chloroacetate reacts with potassium nitrite in concentrated aqueous solution, it produces, when the mixture is heated, a strong reaction with liberation of carbonic acid, and nitromethane distills:

$$Cl.CH^2.CO^2K + KAzO^2 + H^2O = KCl + KHCO^3 + CH^3AzO^2.$$

(Preibisch, *Journ. f. prakt. ch.* (2), t. **8**, p. 316).

I wanted to see if this reaction could be generalized and I first applied it to derivatives of α brominated acids of the aliphatic series.

What are the conditions most conducive to this reaction? By operating with dilute solutions, the hydrolysis reaction:

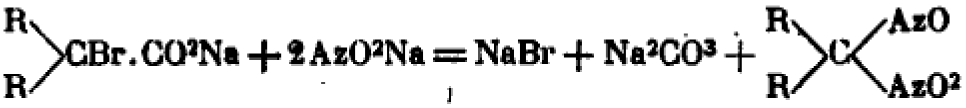
$$R.CHCl.CO^2Na + H^2O = R.CH(OH).CO^2Na + HCl,$$

predominates, and the yield of nitro-derivative is almost zero. It can be made less sensitive by the use of concentrated solutions and a large excess of nitrite, usually 2 moles instead of one. The yield then increases, but never exceeds 50%. With the fatty acids of high molecular weight, the α bromo salt is salted out under the influence of the concentrated solution of nitrite, and much foam is produced at the beginning of the reaction, which cannot be continued.

By operating dry in the presence of only 1 mol. water, the products react abruptly, producing a deflagration which takes the mass to red heat and melts the flask so it is impossible to eliminate the influence of excess water. Another cause of lower yields is the instability of nitromethane in the environment that produced it. Indeed, these derivatives are attacked by hot alkaline solutions, and if they are not removed by distillation as they are formed, they are destroyed on contact with the solution of sodium carbonate remaining in the flask. It is therefore necessary to operate as quickly as possible and slightly superheat the walls of the distillation flask to prevent reflux of the formed product.

The normal chain α brominated acids thus provided me nitroalkanes corresponding to the lower counterpart, by loss of CO_2; but if one operates with acids in which bromine is placed on a tertiary carbon, one obtains only the corresponding pseudonitrole, and with very poor yield.

The reaction can be expressed as follows:



$$\left.\begin{matrix}R\\R\end{matrix}\right> CBr.CO^2Na + 2AzO^2Na = NaBr + Na^2CO^3 + \left.\begin{matrix}R\\R\end{matrix}\right> C \left<\begin{matrix}AzO\\AzO^2\end{matrix}\right.$$

It is evident that the yields are low, pseudonitroles being very unstable in the molten state and not formed in this reaction until about 70°. The formation of nitroalkane has never been observed in this reaction.

α-bromo propionic acid and sodium nitrite: - 20 g of acid are saturated by a 20% solution of potassium carbonate in the presence of phenolphthalein, then 20 g of sodium nitrite, and the liquid forming about 100 cc. is introduced into a distillation flask of 250 cc., and the conducting tube is joined very low for a quick distillation. Around 100 cc. the reaction begins, we remove the flame and continue the distillation after the easing of the first reaction. When no more oily drops pass over, decant the oil distilled, dry over calcium chloride and rectify. Yield 50% of theory.

α-bromo normal butyric acid —

$$CH^3.CH^2.CHBr.\ CO^2H.$$

By operating under the same conditions as above, we obtain nitropropane with 45% of the theoretical yield.

α-bromo isobutyric acid —

$$\begin{matrix}CH^3\\CH^3\end{matrix}\!>CBr.CO^2H.$$

As soon as one starts to heat the solution of the sodium salt with the excess of nitrite, one sees a beautiful blue coloring produced. With distillation, one sees passing a blue oil which quickly solidifies while losing color and which was easy to identify, by the melting point, as isopropyl pseudonitrole

$$\begin{matrix}CH^3\\CH^3\end{matrix}\!>C<\!\begin{matrix}AzO\\AzO^2.\end{matrix}$$

The yield was only 18% of theory, and does not rise if we operate in a current of steam or if you shake the product of the reaction without distillation with ether or benzene, to dissolve the formed pseudonitrole.

bromo-isovaleric acids. — The acid used to prepare bromo derivatives was isovaleric acid of commerce, from the oxidation of amyl alcohol. It contained, therefore, the active acid. After bromination, the mixture of bromo-acids solidified into a crystalline mass and was drained thoroughly. Nitrite was separately reacted with the solid bromo-acid:

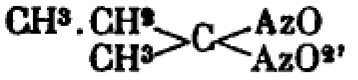
$$\begin{matrix}CH^3\\CH^3\end{matrix}\!>CH\text{-}CHBr\text{-}CO^2H$$

and the liquid part:

$$\begin{matrix}CH^3\\C^2H^5\end{matrix}\!>CBr.CO^2H.$$

The first provided me, while operating as usual, nitro-isobutane; the output was far from satisfactory: 20% only.

The oily portion of the brominated acids subjected to the action of nitrite, after neutralization, gives by heating a blue liquid and distills a minor amount of p-butylpseudonitrole



$$\begin{matrix}CH^3.CH^2\\CH^3\end{matrix}\!>C<\!\begin{matrix}AzO\\AzO^2,\end{matrix}$$

which was identified by its melting point: 58°. The yield was extremely low: about 5%.

α-bromo heptylic acid

$$CH^3(CH^2)^4CHBr.CO^2H.$$

The concentrated solution of the potassium salt is added with 3 mol. of sodium nitrite; the solution must be heated in a quadruple-volume flask, and heating is removed as soon as the reaction starts, to avoid a too abundant foam. The yield is approximately 25%. One manages to increase it up to 35%, while operating in a vacuum of under 100 mm. approximately, and passing a current of steam during the distillation of the nitro. It is necessary to rectify the crude product under vacuum, because it deteriorates always a little at ordinary pressure. The nitrohexane thus obtained must be identical to that which Worstall prepared by oxidizing the hexane (*Am. chem. Journ.*, t. **20**, p. 202). The nitrohexane of Worstall boils at 180-183°; mine at 178-181° (not corr.) and at 78-80° under 15 mm. The density at 0° is 0.953. The detemination of nitrogen provided N 11.5%, theory 10.90%. The liquid remaining in the flask separates in two layers: the upper layer is made of alkali oxyheptylate insoluble in the excess of nitrite; after purification, one can obtain, by crystallization in ligroin, the α-oxyheptylic acid, in superb lustrous spangles, fusible at 65°, as Ley indicates, and not 60°, as Helms said.

α-bromo palmitic acid. — All the tests carried out with this acid failed. On the one hand, the potassium salt of this acid is not very water soluble and insoluble in the solution of nitrite, and on the other hand the formed nitro derivative must have a very high boiling point and be difficult to entrain with the steam. Moreover, an abundant foam occurs as soon as one heats and makes the liquid overflow, whatever the volume of the flask employed.

I intend to test the action of the sodium nitrite on salts of acids brominated in β or γ positions, to see whether, on the one hand, the exchange of Br with NO_2 will occur, and, on the other hand, if the nitrated product obtained keeps its CO_2H group, instead of losing CO_2.