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SOME REACTIONS OF 2-NITROMETHYLQUINOLINE
V. Alkaline Hydrolysis of Halogen Derivatives*

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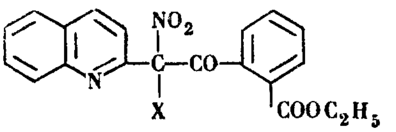
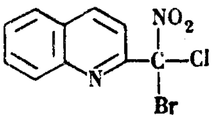
Reactivities of halogens in 2-nitromethylquinoline derivatives are investigated. It is shown that chlorine is more resistant to alkaline hydrolysis than bromine.

The previous paper [1] described a methane derivative with four different substituents, bromine, nitro, α-quinolyl, and o-carboethoxybenzoyl groups (Ia).



I: a X=Br; b X=Cl; c X=H.



II

It was shown that treatment of the compound with bromine led to deacylation and formation of 2-nitrodibromomethylquinoline, and that treatment with alkali led to replacement of a bromine atom by hydrogen (Ic).

The literature contains a number of indications regarding sharp difference in behavior in reactions involving hydrolytic splitting off of chlorine and bromine atoms linked to carbon carrying electronegative substituents [2].

The chloro derivative Ib was synthesized by the present authors. As expected, it underwent alkali-splitting in accordance with another equation, compound Ib being deacylated to give 2-chloronitromethylquinoline. In other words, the order of ease of splitting off of a substituent at the saturated carbon atom of type I compounds is Br > o-carboethoxybenoyl > Cl > NO$_2$, α -quinolyl.

Bromine was the least resistant, and the 1-carboethoxybenzoyl group occupied a position intermediate between the two halogens.

The facility with which chlorine and bromine are replaced by hydrogen in the corresponding dihalogeno derivatives of 2-nitromethylquinoline was previously shown [3]. In the present work the mixed chlorobromo derivative II was synthesized, and in the alkaline hydrolysis of this, the bromine atom was exclusively replaced by hydrogen.

The data obtained are in agreement with the view that the bromine atom has a greater capacity for becoming positively charged than the chlorine atom.

Experimental

Ethyl α -chloro-α-nitro-α-(quinolyl-2)-acetophenone-o-carboxylate (Ib). 2 g (6 mmole) ethyl α-nitro-α-(quinolyl-2)-acetophenone-o-carboxylate (mp 161-162°) was heated and agitated with 56 ml 0.1 N sodium hydroxide solution until solution was complete. A stream of chlorine was passed into the alkaline solution for 10-15 min. The yellow solution completely lost its color. The yellow precipitate was filtered off, washed with water, and dried. Mass 2.1 g, mp 125°. After two recrystallizations from ethanol it had mp 133-134°, mass 1.17 g (53%). Found: Cl 9.35; N 7.23%. Calculated for $C_{20}H_{15}ClN_2O_5$: Cl 8.91; N 7.03%.

Alkaline hydrolysis of the chloro derivative. 1 g (2.5 mmole) Ib was dissolved at room temperature in 75 ml of a 3% ethanolic solution of sodium ethoxide. After a yellow color had appeared, the mixture was neutralized with acetic acid, the ethanol distilled off, and the residue diluted with water. The bright yellow precipitate formed was filtered off, washed with water, and dried. Mass 0.40 g, mp 115°. After three recrystallizations from ethanol it had mp 138°; mass 0.15 g (27%). Found: C 53.72; H 3.63; Cl 15.29; N 12.29%. Calculated for $C_{10}H_7ClN_2O_2$: C 53.93; H 3.15; Cl 15.96; N 12.58%. Mixed mp with authentic 2-chloronitromethylquinoline undepressed.

2-Chlorobromonitromethylquinoline (II). The calculated amount of bromine in glacial acetic acid was added to 2 g (9 mmole) 2-chloronitromethylquinoline [3] which was dissolved, at room temperature, in 200 ml of the same

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*For Part IV see [1].

solvent. The dark brown solution became pale yellow. After five minutes shaking it was diluted with water, when a pale precipitate formed, and this was filtered off, washed with water, and dried, mp 80-81°. Its melting point was unchanged by two recrystallizations from ethanol. Mass 2.26 g (83%). Found: C 39.49; H 2.66; Cl +Br 38.84; N 8.76%. Calculated for $C_{10}H_6BrClN_2O_2$: C 39.80; H 1.99; Cl + Br 38.30; N 9.29%.

Hydrolysis of II. 0.2 g (0.7 mmole) II was refluxed for 1 hr with an aqueous-ethanolic solution of sodium hydroxide. After distilling off the ethanol, the yellow solution was neutralized with dilute acetic acid, and the bright yellow precipitate which formed was filtered off, washed with water, and dried. Mass 0.12 g, mp 133-134°. After being twice recrystallized from ethanol it had mp 138°, mass 0.07 g (48%). Mixed mp with authentic 2-chloronitromethylquinoline undepressed.

Attempt to prepare an iodo derivative. 2 g (4 mmole) ethyl α-bromo-α-nitro-α-(quinolyl-2) acetophenone-o-carboxylate (Ia) was dissolved, by warming slightly, in 400 ml ethanol, and an ethanolic solution of potassium iodide added. Free iodine was liberated, and was removed by adding aqueous sodium thiosulfate solution. After distilling off the ethanol a yellow solution remained. The organic material was extracted with benzene. After distilling off the benzene there remained a dark yellow oily liquid, which quite quickly solidified to yellow crystals. Mass 1.50 g, mp about 148°. After two recrystallizations from ethanol it had mp 160°, mass 0.9 g. Mixed mp of the product with authentic ethyl α-nitro-α-(quinolyl-2)-acetophenone-o-carboxylate undepressed.

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