REFERENCES

1. M. Iaćović, Z. anorg. Chem., 288, 324, 1956.
2. V. P. Davydova, M. G. Voronkov, and B. N. Dolgov, Chemistry and Practical Application of Organosilicon Compounds [in Russian], no. 1, 204, 1957.
3. M. Wieber and M. Schmidt, Z. Naturf., 186, 849, 1963; Angew. Chem., 75, 1116, 1963.
4. R. M. Ismail, Z. Naturf., 186, 1124, 1963.
5. R. M. Ismail, Z. Naturf., 196, 873, 1964; Angew. Chem., 77, 46, 1965.
6. British patent no. 932326, 1961.

15 July 1965

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PREPARATION OF 8-ALKYLAMINOQUINOLINES FROM 8-CHLOROQUINOLINES

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Khimiya Geterotsiklicheskikh Soednenii, Vol. 3, No. 1, pp. 163–164, 1967

UDC 547.831.6+542.958.3

The chlorine of 8-chloroquinoline undergoes a metathetical reaction with methylamine or ethylamine in aqueous solution under pressure in the presence of cuprous chloride, to give 8-methylaminoquinoline and 8-ethylaminoquinoline. The preparation of 8-aminoquinoline from 8-chloroquinoline is confirmed.

Previously S. P. Mitsengendler and one of us developed a method of preparing 8-aminoquinoline (I) from 8-chloroquinoline (II) by the action of aqueous ammonia [1]. Continuing that work, we have prepared from II, by the action of methylamine and ethylamine, 8-methylaminoquinoline and 8-ethylaminoquinoline. Previously these 8-alkylaminoquinolines were obtained by alkylating I [2, 3] (only the picrates had been described).

In a monograph [4] R. Elderfield, referring to his own unpublished results, throws doubt on the results given in [1], since his "experiments on the ammonlysis of 8-halogenoquinolines were unsuccessful, even with an iodo derivative." So we repeated run 4 (optimum) of the paper referred to, and found that using the methods of isolation and purification given in it, I was obtained in yield close to that given.

We did not run a reaction with 8-iodoquinoline, and we cannot say whether it is possible to synthesize I from it. However, the chemist can easily prepare II from the more accessible I, using the results set out in [1].

EXPERIMENTAL

8-Methylaminoquinoline III. 1.34 g freshly-distilled II, 0.13 g CuCl, 10.4 ml 29% aqueous $MeNH_2$, were heated together in a sealed tube for 5 hr at 150°. The products were extracted with ether, the ether distilled off, and the residue vacuum-distilled, bp 90–93° (~1 mm). Yellow liquid, yield 0.78 g (60%).

8-Methylaminoquinoline hydrochloride. Prepared by passing dry HCl gas into an ether solution of III. Red needles ex EtOH, mp 175–184° (decomp.). Found: C 61.90, 61.60, H 5.57, 5.46; Cl 18.38, 18.19; N 14.20; 14.16%. Calculated for $C_{10}H_{10}N_2 \cdot HCl$. C 61.84; H 5.67; Cl 18.27; N 14.43%.

8-Methylaminoquinoline picrate. Prepared by mixing together hot ether solutions of III and picric acid. Orange-red crystals ex EtOH, mp 187–190.5° (decomp.). The literature gives mp 185–186 [2], 187–188° [3]. Found: C 50.13; 49.79; H 3.43; 3.34; N 18.28; 18.14%. Calculated for $C_{10}H_{10}N_2 \cdot C_6H_3N_3O_7$. C 49.63; H 3.38; N 18.08%.

The benzoyl derivative of 8-methylaminoquinoline was prepared by shaking an alkaline emulsion of III with benzoyl chloride. Colorless small tablets from EtOH, mp 139–140°. Found: N 10.45; 10.69%. Calculated for $C_{17}H_{14}N_2O$: N 10.69%.

Benzoyl derivative of 8-ethylaminoquinoline IV. 1.87 g freshly-distilled II, 0.19 g CuCl, 14 ml 33% aqueous $EtNH_2$ were heated together in a sealed tube for 5 hr at 200°. The products were extracted with ether, the extract evaporated, and the residual oil mixed with excess 10% NaOH solution, and benzoylated with benzoyl chloride by the Schotten-Baumann reaction. Yield of impure product 2.2 g (69.5%). After recrystallizing from EtOH, using decolorizing charcoal, it formed slightly yellowish small tablets, mp 135–136°. Found: C 78.89; 78.80; H 5.73; 5.68; N 10.07; 9.80%. Calculated for $C_{18}H_{16}N_2O$: C 78.20; H 5.84; N 10.12%. 8-Ethylaminoquinoline picrate. 0.36 g IV and 7 ml 50% H_2SO_4 were refluxed together for 7 hr 30 min, cooled, and the benzoic acid filtered off. The filtrate was treated with ether, then made alkaline, the amine which separated was extracted with ether, and the extract treated with an ether solution of picric acid. The precipitate weighed 0.33 g (63.5%), and after recrystallizing from EtOH formed orange-red needles mp 175–176° (decomp.). The literature gives mp 173° [2], 180° [3] (decomp.). Found: C 50.66; 50.87; H 3.89; 3.97; N 17.19; 17.23. Calculated for $C_{11}H_{12}N_2 \cdot C_6H_3N_3O_7$. C 50.90; H 3.77; N 17.46%.

8-Aminoquinoline I. 10.1 g freshly-distilled II, 78 ml 30% aqueous ammonia, and 1.01 g CuCl were heated together for 5 hr at 200° in a rotating autoclave. The crude I was filtered off from the ammonia solution. The solid was extracted with ether in a Soxhlet apparatus, and the ammoniacal solution was also extracted with ether. After distilling off the ether, two recrystallizations from petrol ether gave I, 4.72 g (53%). In [1] the content of compound I as found by analysis is given as 69.3%. Glistening pale-yellow crystals, 63.5–64.5°. Found: N 19.31; 19.28%. Calculated for $C_9H_8N_2$. N 19.43%.

REFERENCES

1. N. N. Vorozhtsov, Jr. and S. P. Mitsengendler, ZhOKh, 6, 681, 1936.
2. S. Yoshida, J. Pharm. Soc. Japan., 67, 65, 1947; C. A., 45, 9543, 1951.
3. M. Yasuye and T. Yasukawa, J. Pharm. Soc. Japan., 66, 4, 1946; C. A., 45, 6204, 1951.
4. Heterocyclic Compounds, ed. R. Elderfield [Russian translation], IL, Moscow, 1955.

21 October 1965

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