NOTES

Studies in the Biphenyl Series. V. Bromination of 4-Methoxybiphenyl

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Other investigations in this sequence necessitated repetition of the work of Bell[1] on the bromination of 4-methoxybiphenyl. Our results on the bromination of this ether to mono- and dibrominated products are reported below.

Experimental Part

3-Bromo-4-methoxybiphenyl and 4-Methoxy-4'-bromobiphenyl.—To a solution of 20 g. of 4-methoxybiphenyl in 70 ml. of chloroform, 17.5 g. of bromine in 25 ml. of chloroform was added dropwise during a period of 45 minutes. During this period of time and for an additional 45 minutes the mixture was stirred and maintained at room temperature. Then the chloroform solution was washed with 75 ml. of 10% sodium thiosulfate solution and with 300 ml. of water and dried for 24 hours over anhydrous calcium chloride. The chloroform was removed by distillation and the oily residue was dissolved in ligroin (b.p. 65–110°). On cooling the solution, 21.3 g. of a crystalline mixture was obtained, m.p. 93–104°. Separation of the components of this mixture in a Soxhlet extractor with ligroin (b.p. 45–65°) yielded 6.3 g. (22.1% yield) of 4-methoxy-4'-bromobiphenyl as a residue, m.p. 143–144°,[1] and 3.2 g. (11.2% yield) of 3-bromo-4-methoxybiphenyl, m.p. 78–79°,[1] was obtained from the extract after recrystallization from ethanol.

3,4'-Dibromo-4-methoxybiphenyl.—At room temperature, a solution of bromine (35 g.) in chloroform (25 ml.) was added dropwise, during a period of one hour, to 20 g. of 4-methoxybiphenyl dissolved in 75 ml. of chloroform, to which had been added 0.3 g. of iron powder. In turn, the mixture was refluxed and stirred for 1.5 hours. It was cooled and washed with 75 ml. of 5% sodium thiosulfate solution and then with 300 ml. of water. The total yield of product, m.p. 132–134°,[1] obtained directly and subsequently by crystallization of fractions from ethanol, was 8.5 g. (23% yield). A mixture of equal amounts of the product and 3,4'-dibromo-4-methoxybiphenyl prepared from 3,4'-dibromo-4-hydroxybiphenyl[2] by methylation with methyl sulfate, melted at 133–134°.

Anal. Calcd. for $C_{13}H_{10}OBr_2$: Br, 46.8. Found: Br, 46.2, 46.6.

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(1) Bell, *J. Chem. Soc.*, 1075 (1930). In this article the yields attained in the bromination of 4-methoxybiphenyl were not reported.

(2) Hazlet and Hensley, This Journal, **69**, 708 (1947).

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Received June 2, 1950

Salts of Reinecke Acid with Certain Simple Amines

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The metathetical reaction of amine salts with "Reinecke salt" (ammonium reineckate, $NH_4[Cr(NH_3)_2(SCN)_4]$) in aqueous solution to produce insoluble amine reineckates has been used as a method of isolation of amines.[1] This procedure has been especially useful with certain amino acids and with a few high molecular weight water-soluble bases; *e.g.*, streptothricin. The reineckates are generally rather insoluble in water and recrystallize nicely from aqueous alcohol. Although many of these salts have been reported, in only a few cases have any constants other than analyses and solubilities been determined. The possibility that reineckates might possess melting or decomposition points satisfactory for characterization has led to the examination of a number of these compounds.

The reineckates were prepared by precipitation from aqueous solution and recrystallized from aqueous alcohol. Experimental data on nineteen reineckates are summarized in Table I. It may be seen from these results that the reineckates possess reasonably sharp decomposition ranges, generally between 130 and 230°. Accordingly, it is suggested that reineckates may be of use in the characterization of amines. Mention should be made of the fact that for best results these determinations were carried out in a bath with a heating rate of 6–8° per minute. In many cases, a momentary melting to a clear red liquid just previous to decomposition was noted. A "mixed melting point" using the reineckates of diethanolamine and triethanolamine showed no depression; accordingly, these derivatives are not recommended for such tests of identity. No reineckates could be obtained from the very weak bases piperine, urea and diphenylamine.

Table I

Amine Reineckates

Reineckate	Decomposition point, °C., (uncorrected)	Cr, % Calcd.	Found
Dimethylamine	272–273	14.25	14.42
Ethylamine	231–233	14.25	14.23
Diethylamine	259–261	13.24	13.20
Triethylamine	205–208	12.35	12.50
n-Butylamine	200–204	13.24	13.65
Di-*n*-butylamine	143–146	11.59	11.47
Tri-*n*-butylamine	131–133	10.30	10.33
n-Amylamine	156–158	12.78	13.05
Ethylenediamine	233–240	13.72 (mono) 14.87 (di)	14.01, 14.40
Diethanolamine	162–163	12.26	12.10
Triethanolamine	164–167	11.09	11.30
Creatinine	188–190	12.01	12.09
Glycine ethyl ester	175–178	12.29	12.38
Aniline	195–197	12.65	12.77
Methylaniline	151–152	12.19	12.50
Dimethylaniline	189–191	11.81	12.00
o-Toluidine	133–134	12.19	12.21
Quinaldine	195–198	11.24	11.32
p-Aminoazobenzene	219–220	10.06	10.29

Care must be taken to avoid heating reineckates above about 60° in aqueous or alcoholic solution. Decomposition becomes rapid at higher temperatures. The large temperature coefficient of solubility of all reineckates studied here prevented this limitation from being significant.

The extreme insolubility of reineckates at 0° is shown by experiments carried out upon dilute solu-

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(1) (a) Gmelin-Kraut, "Handbuch der anorganischen Chemie," Vol. III, pt. 1, Carl Winter, Heidelberg, 1912, p. 585; (b) Coupechoux, *J. pharm. chem.*, **30**, 118 (1939); (c) Dakin, *J. Biol. Chem.*, **99**, 531 (1933).