NOTES

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

By John Leo Abernethy and Henry Pollock

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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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).

tions of two amines. The addition of ammonium reineckate solution saturated at 0° to 0.015% aniline hydrochloride or to 0.005% ethylammonium chloride at 0° resulted in the formation of a definite precipitate of the amine reineckate. It would thus appear that the use of ammonium reineckate for the isolation of many amines from very dilute aqueous solutions may be of practical value.

Experimental

Formation of Reineckates.—Hydrochloric acid was added to an aqueous solution or suspension of the amine until the mixture became acidic to congo red. The resulting solution was cooled to room temperature and a filtered, saturated (about 5%) solution of ammonium reineckate was added. Precipitation of the salt began immediately, but the solution was cooled in an ice-bath to improve the yield. The use of an excess (50–100%) of either reagent leads to a significant increase in yield.

Recrystallization.—The reineckates were recrystallized by warming in 70–80% ethyl alcohol to about 60°, filtering, and refrigerating. A few reineckates were sufficiently soluble to make it necessary to use more dilute alcohol. Drying was accomplished over phosphorus pentoxide at room temperature in a vacuum desiccator. Two or three recrystallizations were sufficient to give constant decomposition point and satisfactory analyses.

Analysis.—A weighed sample of the reineckate was heated carefully in a porcelain crucible until the initial vigorous decomposition was complete. The crucible was then ignited with a Meker burner until constant weight was achieved; the residue was weighed as Cr_2O_3. Analyses were run in duplicate and agreed well with theoretical (Table I).

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Alkyl-Substituted Chlorofluoroethanes[1]

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The Prins reaction has recently been extended to include the addition of polyhalo alkanes to polyfluoro alkenes.[2–5] This note describes the aluminum chloride catalyzed condensation of monochloroalkanes with chlorotrifluoroethylene and *unsym*-dichlorodifluoroethylene. The expected products were obtained with poor conversions, and in addition materials were obtained in which the aluminum chloride had substituted chlorine for fluorine in the original addition products.

The Reaction of Isopropyl Chloride and Polyfluoro Olefins.—A mixture of 127 g. of isopropyl chloride, 221 g. of chlorotrifluoroethylene and 25 g. of aluminum chloride was heated to 44° for 18 hours with mechanical shaking. The unreacted olefin was recovered and the residue was washed with water several times, dried over anhydrous sodium carbonate and distilled. Following the removal of the isopropyl chloride there was obtained 10 ml. of material boiling 26–26.2° at 30 mm. (112–113° at 750 mm.) and 2 ml. of material boiling 66–68° at 30 mm. There remained in the still-pot about 3 g. of residues.

The lower boiling material was found to have $n^{25}{}_{D}$ 1.3870, $d^{25}{}_{4}$ 1.3004. *Anal.* Calcd. for $C_5H_7Cl_2F_3$: C, 30.77; H, 3.59; Cl, 36.41; MR_D 35.3. Found: C, 30.24; H, 3.65; Cl, 36.68; MR_D 35.3.

The higher boiling material had $n^{25}{}_{D}$ 1.4078. *Anal.* Calcd. for $C_5H_7Cl_3F_2$: C, 28.37; H, 3.31; Cl, 50.35. Found: C, 29.04; H, 3.55; Cl, 47.76.

A material identical with the higher boiling product was prepared by the aluminum chloride catalyzed condensation of isopropyl chloride with *unsym*-dichlorodifluoroethylene. Therefore it is proposed that the lower boiling material has the structure $(CH_3)_2CHCClFCClF_2$, and the higher boiling the structure $(CH_3)_2CHCCl_2CClF_2$.

Lower reaction temperatures and the use of the "tube" method of Schmerling[6] resulted in the production of a larger proportion of the lower boiling material and a smaller degree of conversion.

The Reaction of *t*-Butyl Chloride and Chlorotrifluoroethylene.—Under the conditions described for the isopropyl chloride reaction, *t*-butyl chloride and chlorotrifluoroethylene gave 5–10% yields of $(CH_3)_3CCClFCClF_2$, b.p. 55–57° at 50 mm., $n^{25}{}_{D}$ 1.4020, and $(CH_3)_3CCCl_2CClF_2$, b.p. 77–80° at 25 mm., $n^{25}{}_{D}$ 1.4405. *Anal.* Calcd. for $C_6H_9Cl_2F_3$: Cl, 33.93. Found: Cl, 34.10. Calcd. for $C_6H_9Cl_3F_2$: Cl, 47.17. Found: Cl, 46.68.

Other Prins Type Reactions Attempted.—Only a trace of reaction could be detected when *n*-butyl chloride was substituted for *t*-butyl chloride.

Allyl chloride could not be used as the alkyl halide because of immediate and extensive polymer formation in the presence of aluminum chloride.

When an attempt was made to use 1-chloro-1,1-difluoroethane as the alkyl halide with chlorotrifluoroethylene only methylchloroform was isolated as a reaction product.

1,2-Dichlorohexafluorocyclobutane and chlorotrifluoroethylene gave no product when heated together in the presence of aluminum chloride. This result was to be expected, since neither of these materials reacted separately with aluminum chloride.

Aluminum bromide could not be used as the catalyst in these reactions, because of its great tendency to substitute bromine for other halogens and because of extensive polymer formation by the alkyl halides in its presence. Stannic chloride and boron trifluoride–ethyl ether did not appear to have catalytic activity.

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(1) This document is based on work performed for the Atomic Energy Commission by Carbide and Carbon Chemicals Division, Union Carbide and Carbon Corporation, Oak Ridge, Tennessee.

(2) Harmon, U. S. Patent 2,404,706, issued July 1946.

(3) Imperial Chemical Industries, Ltd., British Patent 581,254, issued October 1946; *C. A.*, **41**, 2427 (1947).

(4) E. I. du Pont de Nemours and Company, British Patent 581,662, issued October 1946; *C. A.*, **41**, 2427 (1947).

(5) E. I. du Pont de Nemours and Company, British Patent 583,874, issued January 1947; *C. A.*, **41**, 5141 (1947).

(6) Schmerling, THIS JOURNAL, **68**, 1650 (1948).

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Completely Halogenated Ethanes Containing Iodine[1]

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The use of highly fluorinated materials in Grignard syntheses has been relatively unsuccessful, except to give the corresponding fluorohydrocarbon.[2,3] During the course of work here two completely halogenated ethanes containing iodine, 1,2-dichloro-1,1,2-trifluoro-2-iodoethane, and a material thought to be 1-chloro-1,2,2-trifluoro-1,2-diiodoethane, were prepared. Ethereal solutions of both compounds reacted readily with sodium or magnesium, but all attempts to perform a Grignard synthesis were unsuccessful. The Grignard reagent itself apparently was formed by the usual procedure, forming a lower layer in the reaction flask, although there was no evidence of reaction upon the addition of compounds such as benzaldehyde, methyl ethyl ketone or α-naphthyl isocyanate. These compounds al-

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(1) This document is based on work performed for the Atomic Energy Commission by Carbide and Carbon Chemicals Division, Union Carbide and Carbon Corporation, at Oak Ridge, Tennessee.

(2) J. J. Brice, W. H. Pearlson and J. H. Simons, THIS JOURNAL, **68**, 968 (1946).

(3) E. T. McBee and A. Truchan, *ibid.*, **70**, 2910 (1948).