The Preparation and Properties of Alkyl 3-Bromopropionimidate Hydrochlorides

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Alkyl 3-bromopropionimidate hydrochlorides (**1**), prepared from 3-bromopropionitrile, the appropriate alcohol, and hydrogen chloride, were found to have unusual properties. Pyrolysis gave alkyl bromide and 3-chloropropionamide instead of the expected alky chloride and 3-bromopropionamide. Hydrolysis produced alkyl 3-chloropropionate and ammonium bromide as well as alkyl 3-bromopropionate and ammonium chloride. Alcoholysis gave alkyl 3-alkoxy-, 3-bromo-, and 3-chloropropionate, alkyl bromide, dialkyl ether, ammonium chloride, and ammonium bromide. A mechanism is proposed to account for these reactions which postulates elimination of hydrogen bromide from **1** to form the relatively stable, conjugated alkyl acrylimidate cation (**6**). 3-Chloro- and 3-alkoxy-substituted products result from nucleophilic additions of hydrogen chloride and alcohol to this species, and the presence of bromide ion explains the formation of alkyl and ammonium bromides. During alcoholysis, the ortho esters which are produced are converted to normal esters by acid cleavage and elimination of dialkyl ether.

The alcoholysis of alkyl imidate hydrohalides to ortho esters (eq 1) is a well-known reaction[1-3] but it has

$$RC(OR'){=}NH_2^+X^- + 2R'OH \longrightarrow RC(OR')_3 + NH_4X \quad (1)$$

not been applied before to 3-halopropionimidate hydrohalides. We became interested in this as a route to alkyl ortho-3-bromopropionates (**2**) from alkyl 3-bromopropionimidate hydrochlorides (**1**) (eq 2–3).

$$BrCH_2CH_2CN + ROH + HCl \longrightarrow \underset{\mathbf{1}}{BrCH_2CH_2C(OR){=}NH_2^+Cl^-} \quad (2)$$

$$\mathbf{1} + 2ROH \longrightarrow \underset{\mathbf{2}}{BrCH_2CH_2C(OR)_3} + NH_4Cl \quad (3)$$

Alkyl 3-halopropionimidate hydrohalides had been prepared previously from acrylonitrile[4-6] (eq 4) and

$$CH_2{=}CHCN + ROH + 2HX \longrightarrow XCH_2CH_2C(OR){=}NH_2^+X^- \quad (4)$$
$$(X = Cl \text{ or } Br)$$

from 3-chloropropionitrile[5-7] (eq 5) but there is no literature reference to an imidate salt of this type in which

$$ClCH_2CH_2CN + ROH + HCl \longrightarrow ClCH_2CH_2C(OR){=}NH_2^+Cl^- \quad (5)$$

the halogen in the 3 position and the ionic halogen are different. This paper describes the preparation of such compounds (**1**), their alcoholysis, and further experiments suggested by their unusual behavior.

Discussion

The reaction of 3-bromopropionitrile, the appropriate alcohol, and HCl in ether by the classical Pinner method[1-3] (eq 2) gave 80–95% yields of **1**. However, alcoholysis of **1** provided surprising results. Instead of the expected ortho ester (**2**) and ammonium chloride (eq 3), the products were alkyl 3-alkoxy- (**3**), 3-bromo- (**4**), and 3-chloropropionate (**5**), alkyl bromide, dialkyl ether, ammonium chloride, and ammonium bromide.

$$\underset{\mathbf{3}}{ROCH_2CH_2COOR} \qquad \underset{\mathbf{4}}{BrCH_2CH_2COOR} \qquad \underset{\mathbf{5}}{ClCH_2CH_2COOR}$$

For R = CH_3 and C_2H_5, the yields were as follows: 3-substituted propionate esters, 71–73%; ammonium halides, 97–100%; and alkyl bromide (containing a small amount of dialkyl ether), 27–44%.

This development prompted a further examination of the imidate salt starting materials. Halogen analyses eliminated the possibility of a 3-alkoxy-substituted component. Hydrolysis of an imidate hydrochloride normally forms the corresponding ester and ammonium chloride[3] (eq 6) but hydrolysis of **1** gave **5** and NH_4Br in

$$RC(OR'){=}NH_2^+Cl^- + H_2O \longrightarrow RCOOR' + NH_4Cl \quad (6)$$

addition to **4** and NH_4Cl. Pyrolysis of an imidate hydrochloride usually proceeds smoothly to the corresponding amide and alkyl chloride[3] (eq 7) but pyrolysis

$$RC(OR'){=}NH_2^+Cl^- \xrightarrow{\text{heat}} RCONH_2 + R'Cl \quad (7)$$

of **1** gave alkyl bromide and 3-chloropropionamide. Hydrogen halide and a new chloride salt were also produced.

The data indicate that **1** eliminates hydrogen bromide readily to form the alkyl acrylimidate cation **6**. A mechanism which accounts for the observed alcoholysis products on this basis is shown in eq 8–14.

$$\begin{array}{l} BrCH_2CH_2C(OR){=}NH_2^+Cl^- \longrightarrow \\ \qquad CH_2{=}CHC(OR){=}NH_2^+ + Cl^- + Br^- + H^+ \quad (8) \\ \qquad\qquad\qquad \updownarrow \\ \qquad {}^+CH_2CH{=}C(OR)NH_2 \\ \qquad\qquad\qquad \mathbf{6} \end{array}$$

$$\mathbf{6} + ROH \longrightarrow ROCH_2CH_2C(OR){=}NH_2^+ \quad (9)$$

$$\mathbf{6} + HCl \longrightarrow ClCH_2CH_2C(OR){=}NH_2^+ \quad (10)$$

$$-C(OR){=}NH_2^+ + 2ROH \longrightarrow -C(OR)_3 + NH_4^+ \quad (11)$$

$$-C(OR)_3 + HX \longrightarrow -COOR + RX + ROH \quad (12)$$

$$-C(OR_3) \longrightarrow -COOR + R_2O \quad (13)$$

$$NH_4^+ + X^- \rightleftharpoons NH_4X \quad (14)$$

Equation 8 is reasonable, first, in that the relative stability of the conjugated, resonance-stabilized **6** should serve as a driving force for reaction to the right. Second, the reaction mixture in the alcoholysis of **1** was found to be much more acidic than that in the alco-

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(1) H. W. Post, "The Chemistry of Aliphatic Orthoesters," ACS. Monograph Series, No. 92, Reinhold Publishing Corp., New York, N. Y., 1943.

(2) S. M. McElvain, *Chem. Rev.*, **45** (3), 453 (1949).

(3) R. Roger and D. G. Neilson, *ibid.*, **61** (2), 179 (1961).

(4) G. R. Clemo and E. Walton, *J. Chem. Soc.*, 723 (1928).

(5) C. C. Price and J. Zomlefer, *J. Org. Chem.*, **14**, 210 (1949).

(6) G. Braude, *ibid.*, **22**, 1675 (1957).

(7) C. A. MacKenzie, G. A. Schmidt, and L. R. Webb, *J. Amer. Chem. Soc.*, **73**, 4990 (1951).

holysis of unsubstituted alkyl propionimidate hydrochloride. Third, methyl 4-bromobutyrimidate hydrochloride (**7**) undergoes normal alcoholysis into the bromo ortho ester and NH_4Cl (eq 15). This suggests

$$\underset{\mathbf{7}}{BrCH_2CH_2CH_2C(OCH_3){=}NH_2^+Cl^-} + 2CH_3OH \longrightarrow BrCH_2CH_2CH_2C(OCH_3)_3 + NH_4Cl \quad (15)$$

that a bromo substituent causes anomalous reaction only when it is located in the 3 position so that direct dehydrobromination to a conjugated structure is possible.

Nucleophilic additions to **6** of ROH (eq 9) and HCl (eq 10) are analogous to such additions to α,β-unsaturated carbonyl compounds in acidic media where the electron withdrawing character of the C=O group is augmented by acquisition of a proton.[8] As mentioned earlier, alcoholysis of an imidate salt to the orthoester (eq 11) is a familiar reaction. Acid cleavage[1,9,10] (eq 12) and elimination of dialkyl ether[2] (eq 13) as means by which ortho esters are converted to normal esters are also well known. The presence of bromide ion accounts for the formation of NH_4Br (eq 14).

An alternative mechanism which also explains the observed products was considered. In this, the ortho ester **2** is formed (eq 3) and converted into **4** by acid cleavage and ether elimination, **4** loses HBr to form the conjugated alkyl acrylate, and additions of alcohol and HCl to the acrylate yield **3** and **5**, respectively. The scheme was rejected when a model experiment showed that the proposed elimination reaction of **4** does not take place. In the model system, ethyl 3-bromopropionate (**4**, R = C_2H_5) and ethyl orthoformate in ethanolic solution were subjected to the alcoholysis conditions. If elimination of HBr from the bromo ester had occurred, the ortho ester should have been cleaved to ethyl formate and ethyl bromide (eq 12) but only traces of these were found by gas–liquid chromatography.

Methyl 3-chloropropionimidate hydrochloride behaved like **1**, yielding methyl 3-methoxypropionate and methyl 3-chloropropionate on methanolysis.

The hydrolysis products can be explained in a similar manner (eq 8, 10, 14 and 16). Because water has about

$$—C(OR){=}NH_2^+ + H_2O \longrightarrow -COOR + NH_4^+ \quad (16)$$

the same nucleophilicity as the lower alcohols,[11] the 3-hydroxy ester was an expected product by analogy with 3-alkoxy ester formation on alcoholysis, but none was found. Similarly, we did not observe any hydroxy ester in hydrolyzing methyl 3-chloropropionimidate hydrochloride nor did Stevens[12] in the hydrolysis of the 2-methyl homolog of this salt.

The results from the pyrolysis of **1** are consistent with the formation of **6** under these conditions also. The fact that only alkyl bromide (no chloride) was obtained suggests that the alkyl halide which is produced is determined by competition between the halogen anions, the more nucleophilic Br^- winning out. Equation 8 provides the bromide ion required for this and also a source of the hydrogen halide which was observed. Nucleophilic addition of HCl to **6** (eq 10) and decomposition of the resulting imidate to amide account for the 3-chloropropionamide. The other solid product was not identified but appeared to be an imidate hydrochloride. Thus, its aqueous solution gave AgCl on treatment with $AgNO_3$, and ammonia with NaOH. A clear solution was obtained after alkaline hydrolysis and acidification.

There is a possibility that the crystalline imidate salts designated **1** may, in fact, be mixtures of **1** and the 3-chloropropionimidate hydrobromide. In their preparation, the ether solution of reactants remains clear for several hours before the product begins to precipitate. In that interval, the processes of eq 8 and 10 might take place to yield a mixture of the two salts. However, the crystals are well-formed, uniform needles and melt sharply, suggesting pure compounds. We believe that the products are largely **1** and that dissociation according to equation 8 is appreciable only on dissolving the salt in a highly polar solvent or on melting.

Experimental Section

Materials.—Alcohols were dried over the corresponding magnesium alkoxides[13] before use. The nitriles were commercial products which were not purified further.

Methyl 3-methoxy- and 3-chloropropionate were prepared from 3-methoxy- and 3-chloropropionitrile, respectively, by conversion into the methyl imidate hydrochlorides and hydrolysis. Methyl and ethyl hydracrylate were obtained from hydracrylonitrile in a similar manner, essentially by the procedure of Fein and Fisher.[14] As reported by these authors, ethyl 3-chloropropionate was a byproduct in the synthesis of ethyl hydracrylate. The other 3-substituted methyl and ethyl propionates used as glpc standards were commercial products.

Gas–Liquid Partition Chromatography.—Conditions common to all runs were: Aerograph Hy-Fi chromatograph, Model 600-D; flame ionization detector; carrier gas, N_2 (25–30 ml/min); sample size, 0.7 μl of a 1–2% solution in CS_2; solid support, 60–80 mesh Chromosorb W.

A 5 ft × 0.125 in. 5% SE-30 silicone column at 121° was used for methyl ortho-4-bromobutyrate but produced severe tailing of peaks for the other mixtures. Accordingly, they were run in a 4 ft × 0.125 in. 10% Carbowax column, the alcoholysis products at 82° and the hydrolysates at 119° (hydracrylates have long retention times). The relative response of the detector toward alkyl 3-alkoxy-, 3-chloro-, and 3-bromopropionate was determined on known mixtures for R = CH_3 and C_2H_5 so that reliable measurements of yields could be made from peak areas.

Alkyl Imidate Hydrochlorides.—Ethyl propionimidate hydrochloride was synthesized by the method of McElvain and Nelson.[15]

In a typical preparation of the other imidate salts, a solution of 0.20 mol of nitrile and 0.20 mol of the anhydrous alcohol in 100 ml of dry ether was cooled in ice with exclusion of moisture ($CaCl_2$ tube). Dry HCl was passed in until about 0.4 mol had been absorbed.[16] After standing in the refrigerator for several days, the precipitated product was filtered, washed with anhydrous ether, and vacuum dried in a desiccator over H_2SO_4 and KOH.

For the 3-bromopropionimidate hydrochlorides, direct titration of chloride ion with aqueous $AgNO_3$ (Mohr method) invariably gave high values indicating that part of the bromine was also reacting. Accordingly, total halogen was determined by converting the bromine to bromide ion with hot 10% aqueous NaOH before titration.

Methyl 3-bromopropionimidate hydrochloride showed a marked tendency to form amide by loss of methyl halide. For ex-

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[8] E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart, and Winston, Inc., New York, N. Y., 1959, p 528.

[9] S. M. McElvain and J. P. Schroeder, *J. Amer. Chem. Soc.*, **71**, 40 (1949).

[10] S. J. Fitch, *ibid.*, **86**, 61 (1964).

[11] K. B. Wiberg, "Physical Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1964, pp 421–423.

[12] C. L. Stevens, *J. Amer. Chem. Soc.*, **70**, 165 (1948).

[13] K. B. Wiberg, "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 242.

[14] M. L. Fein and C. H. Fisher, *J. Org. Chem.*, **13**, 749 (1948).

[15] S. M. McElvain and J. W. Nelson, *J. Amer. Chem. Soc.*, **64**, 1825 (1942).

[16] While only a stoichiometric amount of HCl is necessary, a large excess increases the reaction rate with no apparent deleterious effect.

TABLE I

ALKYL IMIDATE HYDROCHLORIDES, $RC(OR'){=}NH_2{}^+Cl^-$

R	R′	Registry no.	Nitrile (and alcohol), mol	HCl, mol	Reaction time, days	Yield, %	Mp, °C	Total halogen, equiv/mol Calcd	Total halogen, equiv/mol Found
$BrCH_2CH_2$	CH_3	21367-84-0	0.20	0.37	6	89.5	70.5–72 dec	2.00	1.95
			0.20	0.21	5	60			
$BrCH_2CH_2$	C_2H_5	21369-85-1	0.20	0.37	7	87	96.5–98.5 dec	2.00	2.01
			0.20	0.22	9	68	96.5–98.5 dec		
			0.10	0.13	1	52	97.5–98.5 dec		
			0.10	0.30	7	95			
$BrCH_2CH_2$	n-C_3H_7	21367-86-2	0.10	0.35	7	94.5	103–104 dec	2.00	2.04
			0.20	0.33	9	84			
$BrCH_2CH_2$	n-C_4H_9	21367-87-3	0.050	0.1	5	65	103–103.5 dec	2.00	2.03
			0.20	0.26	5	73	101.5–102 dec		
$ClCH_2CH_2$	CH_3	21367-88-4	0.10	0.2	6	86	75.5–77.5 dec[a]	2.00	2.00
$ClCH_2CH_2$	C_2H_5	21367-89-5	0.10	0.23	2	80	106–107 dec[b]	2.00	[c]
$BrCH_2CH_2CH_2$	CH_3	21367-90-8	0.050	0.12	7	84		2.00	[d]

[a] Reported[5] to melt at 93–94°. [b] Reported[4] to melt at 109°. [c] Per cent chloride ion: calcd, 20.6; found, 21.3. [d] Per cent chloride ion: calcd, 16.4; found, 17.2.

ample, on standing for 2 months in a desiccator, a sample went completely to amide, mp (after recrystallization from benzene) 107–108° (lit.[17,18] mp 116° for $BrCH_2CH_2CONH_2$; lit. mp 102.5°,[1] 103°[19] for $ClCH_2CH_2CONH_2$). The higher homologs were more stable and could be stored for weeks without apparent change so long as moisture was excluded.

The experimental data for the imidate hydrochloride syntheses are summarized in Table I.

Ethanolysis of Ethyl 3-Bromopropionimidate Hydrochloride.—17.7 g (0.082 mol) of the salt was dissolved in 200 ml absolute ethanol and the mixture allowed to stand for one day at room temperature. The liquid was decanted from precipitated ammonium halide and fractionally distilled to give a forerun, bp 39–75°, and ethanol, bp 75–78°. Addition of dry ether to the residue completed the precipitation of ammonium halide which was recovered by filtration. Vacuum distillation of the filtrate gave 8.67 g of liquid, bp 75–80° (25 mm), n^{20}_{D} 1.4172, d^{20}_{4} 1.037.

The yield of ammonium halide was 6.47 g (theory for NH_4Cl 4.37 g, for NH_4Br 8.01 g). The silver halide obtained by treatment of this product in aqueous HNO_3 with $AgNO_3$ was only partly soluble in 4*M* aqueous ammonia and the insoluble part was yellow, showing the presence of AgBr as well as AgCl. A semiquantitative determination of the individual silver halides in this way indicated that 0.045 mol of NH_4Cl and 0.034 mol of NH_4Br were produced in the alcoholysis.

The forerun, bp 39–75°, was washed with water to give 2.15 g of crude ethyl bromide, bp 37–38.5°, n^{27}_{D} 1.4086, d^{20}_{4} 1.335. The aqueous washings had the odor of diethyl ether. In another alcoholysis, this volatile fraction was found to have an ir spectrum almost identical with that of a known ethyl bromide (90%)–ethanol (5%)–diethyl ether (5%) mixture, and reaction with aqueous $AgNO_3$ gave yellow AgBr in an amount corresponding to 80% ethyl bromide. In a third run, provision was made for trapping ethyl chloride but none was found.

The liquid boiling at 75–80° (25 mm) was shown to be a mixture of ethyl 3-ethoxy-, 3-chloro- and 3-bromopropionate. The ir spectrum, boiling range, n_{D} and d were consistent with such a composition and glpc gave three peaks with the same retention times as authentic samples of these esters. Alkaline hydrolysis followed by gravimetric determination of halogens as silver halides indicated 0.042 mol of ethoxy-, 0.012 mol of chloro- and 0.005 mol of bromo ester. The comparable values from glpc peak areas were 0.038, 0.011, and 0.009 mol. Treatment of the ester mixture with anhydrous K_2CO_3 and absolute ethanol gave as the sole organic product ethyl 3-ethoxypropionate,[20-22] bp 82–83° (31–32 mm), n^{20}_{D} 1.4088, d^{20}_{4} 0.964, sapon equiv 139 (calcd 146). This compound was further characterized by glpc retention time, ir spectrum, and hydrolysis to the acid from which the *p*-bromophenacyl ester, mp 48–50° (lit. mp 48°,[23] 56°[24]) was made.

Methanolysis of Methyl 3-Bromopropionimidate Hydrochloride.—The procedure was similar to that above except the reaction was run in the refrigerator to minimize amide formation. Methanolysis of 34.2 g (0.169 mol) of the imidate salt for 1 week gave (cold trap) 4.3 g of crude methyl bromide, bp −6 to 7°. By analogy with the ethanolysis results, the low boiling impurity was probably dimethyl ether. The ammonium halide product amounted to 12.15 g (calcd for NH_4Cl 9.04 g, for NH_4Br 16.6 g) and a total halogen determination (Mohr method) indicated a quantitative yield. Distillation of the filtrate from the ammonium salts gave 16.84 g of liquid, bp 62–77° (30 mm), n^{20}_{D} 1.4265, d^{20}_{4} 1.213, which was shown to be a mixture of methyl 3-methoxy-, 3-chloro-, and 3-bromopropionate by the same types of evidence used to identify the analogous mixture of ethyl esters in the preceding experiment. The composition from glpc peak areas was 0.039 mol of methoxy-, 0.039 mol of chloro-, and 0.045 mol of bromo ester. Treatment of the mixture with anhydrous K_2CO_3 and absolute methanol gave as the only organic product methyl 3-methoxypropionate,[20-22] bp 60–61° (30–31 mm), n^{20}_{D} 1.4020, d^{20}_{4} 1.003, sapon equiv 114 (calcd 118), which was further characterized by glpc retention time, ir spectrum, and hydrolysis to the acid. The *p*-bromophenacyl ester of the latter had mp 68.5–70.5° (lit.[24] mp 70°).

Alcoholysis of Other 3-Halopropionimidate Hydrochlorides.—*n*-Propyl and *n*-butyl 3-bromopropionimidate hydrochloride, on reaction with the corresponding absolute alcohol at room temperature, also gave yields of ammonium halide between those calculated for NH_4Cl and NH_4Br. The ethereal filtrates from the ammonium halides were placed over anhydrous K_2CO_3 for several days before distillation.[25] In both experiments the product was the alkyl 3-alkoxypropionate. If halo esters were formed, they were apparently converted to the alkoxy ester by reaction with alcohol in the presence of the K_2CO_3. The ir spectra of both esters were consistent with the assigned structures. Additional data are summarized below.

n-Propyl 3-*n*-propyloxypropionate[20-22] was obtained in 62% yield, bp 85–88° (11 mm), n^{20}_{D} 1.4152, d^{20}_{4} 0.929, sapon equiv 176 (calcd 174). The amide, mp 49–52° (lit.[27] mp 52°), and

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[17] H. W. Johnson, Jr., and D. E. Bublitz, *J. Amer. Chem. Soc.*, **79**, 753 (1957); *ibid.*, **80**, 3150 (1958).

[18] J. C. Martin and P. D. Bartlett, *ibid.*, **79**, 2533 (1957).

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[20] A. Karvonen, *Ann. Acad. Sci. Fennicae*, **10A** (6), 1 (1916); "Beilstein's Handbuch Der Organischen Chemie," 4th ed, 1st suppl., Vol. III, Springer-Verlag, Berlin, 1929, pp 112–113.

[21] C. E. Rehberg, M. B. Dixon, and C. H. Fisher, *J. Amer. Chem. Soc.*, **68**, 544 (1946).

[22] T. L. Gresham, J. E. Jansen, F. W. Shaver, J. T. Gregory, and W. L. Beears, *ibid.*, **70**, 1004 (1948).

[23] R. V. Christian, Jr. and R. M. Hixon, *ibid.*, **70**, 1333 (1948).

[24] G. F. Hennion and F. D. Kupiecki, *J. Org. Chem.*, **18**, 1601 (1953).

[25] This technique of neutralizing acids before distillation of an ortho ester is often effective in minimizing decomposition to the normal ester.[9,26] It was also tried in the alcoholyses with methanol and ethanol. In all instances, only normal esters were obtained indicating that, even before workup, there were no ortho esters present.

[26] S. M. McElvain and R. L. Clarke, *J. Amer. Chem. Soc.*, **69**, 2661 (1947).

[27] S. Kilpi, *Z. Phys. Chem.*, **80**, 165 (1912).

p-bromophenacyl ester, mp 61–62° (lit. mp 58°,[23] 60°[24]), were prepared as derivatives.

n-Butyl 3-*n*-butyloxypropionate[21,22] was obtained in 51% yield, bp 91–92° (3.5 mm), $n^{20}{}_{\mathrm{D}}$ 1.4223, $d^{20}{}_4$ 0.911, sapon equiv 198 (calcd 202). A small amount of acrylamide, mp 83–84° (lit.[28] mp 84.5°), codistilled with the ester and was identified from its ir spectrum.

Methanolysis of 5.32 g (0.0336 mol) of methyl 3-chloropropionimidate hydrochloride in the refrigerator for 2 days gave 1.84 g (100%) NH_4Cl and 2.00 g of liquid, bp 62–65° (32 mm), $n^{20}{}_{\mathrm{D}}$ 1.4036, $d^{20}{}_4$ 1.044, which was shown by glpc to be a 73:27 (by weight) mixture of methyl 3-methoxypropionate (0.0124 mol) and methyl 3-chloropropionate (0.0044 mol).

Methanolysis of Methyl 4-Bromobutyrimidate Hydrochloride.—A solution of 8.5 g (0.039 mol) of the imidate salt in 50 ml of absolute methanol was kept in the refrigerator for 5 days. The precipitated NH_4Cl (1.0 g, 0.019 mol) was filtered and the filtrate made alkaline to phenolphthalein with 0.021 mol of methanolic NaOMe.[25] Distillation gave 5.4 g (61%) of methyl ortho-4-bromobutyrate, bp 85–95° (15 mm), $n^{20}{}_{\mathrm{D}}$ 1.4563, $d^{20}{}_4$ 1.370, 34.8% Br (calcd 35.2). The product displayed a carbonyl absorption at 1740 cm^{-1} in the ir and glpc showed 5% lower boiling impurity, presumably the normal ester.

Hydrolyses of Imidate Hydrochlorides.—To an ice-cooled slurry of 15.3 g (0.076 mol) of methyl 3-bromopropionimidate hydrochloride in 35 ml of ether was added 1.51 g (0.084 mol) of water with stirring over a 15-min period. Stirring was continued for an additional 30 min and the mixture placed in the refrigerator overnight. The ether solution was decanted from the insoluble solid and distilled to give 9.29 g of liquid, bp 71–80° (32 mm), $n^{20}{}_{\mathrm{D}}$ 1.4455, $d^{20}{}_4$ 1.393, which was found by glpc to be a 70:30 (by weight) mixture of methyl 3-bromopropionate (0.039 mol) and methyl 3-chloropropionate (0.023 mol). The yield of ammonium halide was 5.76 g (calcd for NH_4Cl 4.05 g, for NH_4Br 7.40 g). Both AgCl and AgBr were obtained by treatment of the salt in aqueous HNO_3 with $AgNO_3$. The toal yield of ammonium halide was 94% (Mohr method).

Ethyl 3-bromopropionimidate hydrochloride was hydrolyzed in dioxane solution with a 20-fold molar excess of water and also in aqueous solution (0.050 mol in 100 ml of water). In both cases, the product was a 55:47 (by weight) mixture of the bromo and chloro esters.

In none of the three hydrolyses was there any evidence of alkyl hydracrylate by glpc.

Pyrolysis of Ethyl 3-Bromopropionimidate Hydrochloride.—7.38 g (0.0341 mol) of the imidate salt was heated at 110–113° in a distillation apparatus with an ice-cooled receiver and a cold trap in Dry Ice–acetone to condense ethyl chloride. The salt melted with decomposition and 2.68 g (72%) of crude ethyl bromide, bp 34–35°, $n^{25}{}_{\mathrm{D}}$ 1.4145, $d^{20}{}_4$ 1.38, distilled into the receiver but no ethyl chloride was found in the cold trap. Both receiver and trap contained hydrogen halide (odor, fuming in moist air).

The pale yellow residual oil (4.49 g) became a waxy solid on cooling. Repeated extraction with boiling benzene left 2.68 g of an ethanol- and water-soluble solid. Treatment of its aqueous solution with $AgNO_3$ and HNO_3 gave a heavy precipitate of silver halide which darkened rapidly indicating it to be AgCl. Another portion of the aqueous solution was made strongly basic with NaOH and boiled until ammonia evolution had subsided. On acidification, the residual solution remained clear.

Concentration and cooling of the benzene extract precipitated 1.10 g of 3-chloropropionamide, mp 100.5–102.5° (lit. mp 102.5°,[5] 103°[19]).

Acidity of Alcoholysis Reaction Mixtures and Related Solutions.—The pH values determined (glass electrode) for absolute ethanol and 0.03 *M* solutions of various pertinent substances in this solvent are shown in Table II.

TABLE II

Solute	pH
None	5.4
NH_4Cl	3.6
NH_4Br	3.1
CH_3COOEt	5.2
$ClCH_2CH_2COOEt$	3.4
$BrCH_2CH_2COOEt$	3.7
$BrCH_2CH_2C(OEt){=}NH_2{}^+Cl^-$	2.0 (3 min)
	0.9 (61 min)
	0.6 (317 min)
	0.8 (95 hr)
$CH_3CH_2C(OEt){=}NH_2{}^+Cl^-$	2.9 (2 min)
	2.3 (52 min)
	2.0 (143 min)
	2.0 (19 hr)

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Arylation of Aromatic Compounds by Electrochemical Reduction of Benzenediazonium Tetrafluoroborate in Aprotic Solvents

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Benzenediazonium tetrafluoroborate has been reduced electrolytically at 0 V *vs.* sce in aprotic solvents to produce a free phenyl radical. The phenyl radical so formed has been used for phenylation of benzene, toluene, anisole, benzonitrile, nitrobenzene, bromobenzene, and naphthalene. The isomer ratios, total rate ratios, and partial rate factors agree with those obtained using benzoyl peroxide or N-nitrosoacetanilide as sources of free radicals and demonstrate that the mechanism of phenylation is completely free radical.

Arylation of aromatic substrates by homolytic substitution was first carried out by Kuhling[1] and Gomberg and coworkers.[2] Subsequently a vast literature has arisen on the nature of the reactions involved in homolytic aromatic substitution together with the results of quantitative measurement of isomer ratios. The present position on most of these reactions has been summarized by Williams[3] and Hey.[4]

The possibility of producing free aryl radicals by direct electrolytic reduction of diazonium cations by a single electron step was raised by the discovery of their polarographic activity.[5,6] Kochi[7] attempted to correlate the half-wave potentials of diazonium salts

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