ment inaltere sous l'influence de l'acide cyanhydrique à froid, en présence ou en l'absence de solvants."

An explanation of Delépine's failure to effect the addition of prussic acid in the case cited above has now been found. The prussic acid employed by Bailey and Snyder contained a very small amount of hydrochloric acid which had been added to the stock bottle to prevent polymerization and no thought was given to the possible effect this might have in the reaction. We now find, in conformity with Delépine's observation, that prussic acid is without effect on methyleneaminoacetonitrile. However, if the prussic acid contains a little hydrochloric acid, iminoacetonitrile is formed in quantitative yield. In one experiment 225 cc. of absolute HCN were distilled onto 150 g. of $CH_2 = NCH_2CN$. After standing 48 hours the prussic acid was distilled off and the residue proved to be unchanged starting material. The regained prussic acid with the addition of 6 drops of concentrated hydrochloric acid was again placed on the methyleneaminoacetonitrile, allowed to stand 48 hours, and then distilled off at 50°. It was then found that the conversion of the methylene compound to iminoacetonitrile was complete.

AUSTIN, TEXAS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON.]

THE ACTION OF BENZENESULFONYLCHLORIDE ON ORGANIC BASES IN ANHYDROUS ETHER.

BY GEORGE L. SCHWARTZ AND WILLIAM M. DEHN.

Received August 10, 1917.

These studies were undertaken primarily for the purpose of throwing light on the mechanics of organic reactions in anhydrous ether. Various halides previously[1] were found to yield with organic bases simple additive products. This type of reaction was especially marked in cases of acetyl chloride[2] and benzoyl chloride,[3] which yielded additive products not only with primary and secondary bases but also with tertiary bases.

General conclusions in agreement with previous studies, involving reactions of acyl halides on organic bases and obtained by these studies with benzenesulfonylchloride, are as follows: 1. Sunlight promoted all of these reactions. 2. The initial reactions were uniformly additive. 3. The reactions were non-ionic. 4. Some of the additive compounds formed directly could not be obtained by the action of hydrogen chloride on the respective substituted benzenesulfones.

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[1] THIS JOURNAL, 33, 1588, 1598 (1911); 34, 286, 290, 1399, 1409 (1912); 36, 2091 (1914); 37, 2122 (1915); 39, 1717 (1917).

[2] *Ibid.*, 34, 1399 (1912).

[3] *Ibid.*, 36, 2091 (1914).

Beyond the fact that direct sunlight also accelerated the reactions with benzenesulfonylchloride, as with previously studied reactions in anhydrous ether, no new observations of the influence of light were made.

Whereas the additive compounds were formed in accordance with the reaction

I. $C_6H_5SO_2Cl + RNH_2 \longrightarrow C_6H_5SO_2.RNH.HCl$

and these were always the initial products, yet with primary and secondary bases almost always other reactions

II. $C_6H_5SO_2.RNH.HCl \longrightarrow C_6H_5SO_2.RNH + HCl$

III. $RNH_2 + HCl \longrightarrow RNH_2.HCl$

promoted by heat, by traces of water, and by free base, gave mixtures of the additive compound and the hydrochloride of the base used. These successive reactions are indicated in the following combined equation:

IV. $C_6H_5SO_2Cl + 2RNH_2 \longrightarrow C_6H_5SO_2.RNH.HCl \longrightarrow$
$C_6H_5SO_2.RNH + RNH_2.HCl$

Evidences that the additive compounds were formed and that they were the initial products were obtained by the following methods:

1. By the use of sufficient ether, unchanged original substances and all products except the additive compounds and the hydrochlorides of the original base were held in solution. *Any precipitate whatsoever indicated a reaction,* and whether the precipitate was purely the additive product, the hydrochloride of the original base, or a mixture of the two, was determined by analysis.
2. Microscopical examination of the crystals forming in the anhydrous ether revealed one or more forms.
3. Melting-point determinations of the ether-insoluble products generally indicated their true nature.
4. Spinning motions of the ether-insoluble products on water generally indicated mixtures.
5. Halogen analysis of the ether-insoluble products demonstrated their exact composition.

These methods have enabled us to detect the additive compounds of organic bases, even when such additive compounds could not be separated from mixtures obtained. In some cases, these mixtures were recrystallized and then gave pure products. In other cases, complete analyses[1] revealed the true proportion of the components.

Since tertiary bases contain no labile hydrogen atoms, addition only is possible with them,[2] in accordance with the following types:

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[1] This Journal, 36, 2087 (1914).

[2] With CBr_4 and tertiary bases, types (*a*) and (*d*) were obtained. This Journal, 33, 1594–1596 (1911). With C_2I_2, type (*d*) was obtained. *Ibid.*, 33, 1599 (1911). With C_2I_4, types (*a*) and (*d*) were obtained. *Ibid.*, 34, 293, 295 (1912). With CHI_3, types (*a*), (*b*) and (*c*) were obtained. *Ibid.*, 34, 1413 (1912). For some preliminary studies with diphenylureachloride and tertiary bases, see *Ibid.*, 37, 2130 (1915).

(*a*) $C_6H_5SO_2Cl.R_3N$
(*b*) $C_5H_6SO_2Cl(R_3N)_2$
(*c*) $C_5H_6SO_2Cl(R_3N)_3$
(*d*) $(C_6H_5SO_2Cl)_2R_3N$

We found that benzenesulfonylchloride yielded with tertiary bases additive compounds of the types (*a*) and (*b*), thus differing from acetylchloride[1] and benzoylchloride[2] which gave additive compounds of type (*a*) only.

With traces of moisture present in the materials used, traces of the hydrochloride of the base may be obtained, in accordance with the following reaction

$$\text{VI. } C_6H_5SO_2Cl.R_3N + H_2O \longrightarrow C_6H_5SO_2OH + R_3N.HCl$$

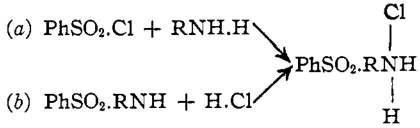
and these products may yield the halogen-free salt, in accordance with the reaction

$$\text{VII. } C_6H_5SO_2OH + R_3N \longrightarrow C_6H_5SO_2OH.R_3N.$$

In consequence of these reactions, the precipitates were not always pure additive compounds. Furthermore, when the end product of reaction is of types (*b*) or (*c*), early formed precipitates may also contain (*a*) and (*b*), for it must be concluded that one molecule of the base first adds, then the second molecule, and finally and possibly, the third molecule.

That the reactions are non-ionic, as well as additive, is proven in the same manner as in previous studies[3] and especially by the remarkable, previously observed[4] phenomenon of the non-interchangeability of parts of the additive, pentavalent nitrogen compounds. For example, benzenesulfonylchloride yields the additive compound with aniline, and the toluidines, but hydrogen chloride fails absolutely to yield with their corresponding tertiary nitrogen compound the same or any additive compound.

The hypothesis previously proposed to account for these facts is especially applicable to the benzenesulfonylchloride derivatives. For example, in the reactions



$$\left.\begin{array}{l}(a)\ PhSO_2.Cl + RNH.H \\ (b)\ PhSO_2.RNH + H.Cl\end{array}\right\} \rightarrow PhSO_2.R\overset{\displaystyle Cl}{\underset{\displaystyle H}{N}}H$$

the first case (*a*) necessitates a break between RSO_2 and Cl and the second case (*b*) necessitates a break between H and Cl. Now the former break

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[1] This Journal., 34, 1407 (1912).

[2] *Ibid.*, 36, 2100 (1914).

[3] *Ibid.*, 33, 1589 (1911); 36, 2094 (1914); 37, 2124 (1915).

[4] *Ibid.*, 36, 2095 (1914); 37, 2124 (1915).

certainly is easier than the latter, since by heat alone the former compound is far more easily decomposed than is the latter. Since the latter fails absolutely to yield the additive compound, the conclusion is inevitable that HCl does not ionize in absolute ether and *the additive reactions are non-ionic.*

The method of preparation of products was the same as previously employed in other studies of organic reactions in anhydrous ether. The ether itself was distilled first from sodium and finally from phosphoric anhydride into receivers freed from atmospheric moisture. Stock solutions of benzenesulfonylchloride in the anhydrous ether were prepared and distributed into bottles of convenient size. These bottles were stoppered immediately and their contents were protected as carefully as possible from any subsequent contact with atmospheric moisture. Each bottle contained 1 g. of benzenesulfonylchloride and 90 cc. of ether. As desired, the equimolecular quantities of the respective organic bases were added, and the progress of the reactions during a number of days or weeks in diffused or direct sunlight was observed. After sufficient time the precipitates were filtered on a Büchner funnel, washed with anhydrous ether, dried in desiccators, and analyzed.

The percentages of chlorine of the respective mixtures enabled us to calculate[1] the two hydrochlorides contained therein. The additive compound thus calculated will be indicated (A C, 43.29%).

Primary Bases.

Aniline.—When 1 g. of benzenesulfonylchloride and 0.53 g. of aniline were dissolved in 90 cc. of anhydrous ether, no immediate precipitate was formed, but during a number of days rectangular plates and hexagonal prisms with pyrimidal ends were precipitated. After filtering different samples and washing with anhydrous ether, the following analyses were made:

Preparations. Found.	I. 11 days.	I. 15 months.	I. Recrystallized from $C_2.H_5OH$.	II. 3 months.
% Cl	17.09	20.94	23.51	25.42
M. p.	188.0°	...	190.0°	191.0°

	Calculated for	
	$C_6H_5NH_2HCl$.	$C_6H_5NH_2.C_6H_5SO_2Cl$.
% Cl	27.35	13.15
M. p.	192.0	...

These data indicate that the precipitates were mixtures of *benzene sulfonylanilidehydrochloride* and anilinehydrochloride.[2] That benzenesul-

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[1] For example see the data of *o*-toluidine. Calc.: 12.48% Cl and 24.70% Cl. Found: 19.41% Cl. The difference between the former two is 12.22; the difference between the latter two is 5.29; and 5.29/12.22 of 100 = 43.29% of the additive product.

[2] $C_6H_5NH_2.HCl$ m. p. 192°. Pinner, *Ber.*, 14, 1083 (1881). Ullmann gives 198°, *Ber.*, 31, 1691 (1898).

fonylanilide[1] was not present in the precipitate was proven by a determination of its solubility in ether—30 g. in 100 cc. at room temperature. Evidently 18 times the ether, necessary to keep the anilide in solution, was used.

The original ether solution yielded benzenesulfonylanilide—after filtering, washing with dilute potassium hydroxide solution, acidifying with dilute hydrochloric acid, washing with water, drying with calcium chloride, and evaporating the ether. Crystals of the known m. p. 110° were obtained.

Benzenesulfonylanilide may be prepared by the direct action of aniline and benzenesulfonylchloride. Heat is produced by their union and a semisolid mass is formed. If warmed with alkalies, to decompose unchanged chloride, then acidified to precipitate the aniline and to dissolve the aniline, the pure anilide is obtained.

When equimolecular quantities of aniline and benzenesulfonylchloride were heated, and the resulting mass was repeatedly extracted with ether, to remove benzenesulfonylanilide and unchanged original materials, an insoluble residue, consisting of glistening flakes and melting at 188°, was obtained. It contained 25.13% Cl, thus indicating that 15.87% of the additive compound survived the conditions of the experiment.

When two molecular parts of aniline and one molecular part of the chloride were brought together, the temperature rose to 110°. After washing with ether, the residue contained 25.22% Cl or 15.27% of the additive compound.

These experiments prove that the additive compound is formed even by direct contact and that it is fairly stable towards heat. That the additive compound cannot be formed by the action of hydrogen chloride on benzenesulfonylanilide was proven by the experiment of treating anhydrous ether and toluene solutions of the latter with hydrogen chloride. No precipitates were formed even after months of standing.[2]

The latter experiments lead to the conclusion that the reactions are not ionic; the former experiments lead to the conclusion that the reactions are additive.

o-Toluidine.—The mixture remained clear for some time; after one month, dark, wart-like clumps of crystals were observed; after two months,

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[1] Biffi, *Ann.*, 91, 107 (1854); Geriche, *Ibid.*, 100, 217 (1856); Wallach, *Ibid.*, 214, 221 (1882); Brugnatelli, *J. prakt. Chem.*, [2] 47, 368 (1893); *Z. Kryst. Min.*, 30, 191; Meyer and Ascher, *Ber.*, 4, 326 (1871).

[2] The failure to obtain analogous additive compounds by the action of hydrogen chloride on the trivalent-nitrogen substituted compounds was previously observed by Dehn and Ball and by Dehn and Platt. THIS JOURNAL, 36, 2095 (1914); 37, 2124 (1915). This same phenomenon was observed in these studies with the anilide and the toluides.

light-colored needles separated; after five months, the crystals melted[1] at 211.0° and contained 19.41% Cl.

Calc. for $CH_3C_6H_4NH_2.C_6H_5SO_2Cl$: Cl, 12.50%.
Calc. for $CH_3C_6H_4NH_2.HCl$: Cl, 24.69%.

Estimated ratio of the former in the mixture, 43.0%.

m-Toluidine.—The solution remained clear for hours; after a number of days a moss-like mass of microscopic crystals, melting[2] at 185° and containing 21.94% Cl, was obtained (A. C. 22%). The ether solution yielded *benzenesulfonyl-m-tolylamide*, coarse prisms from CCl_4, melting at 95° and soluble 19 parts in 100 parts of ether. This compound was also prepared by the direct action of *m*-toluidine on benzenesulfonylchloride in the manner indicated under aniline.

p-Toluidine.—Heavy precipitates[3] were formed at once and contained, respectively:

1/2 hour....................	24.62% Cl or 0.6% of the additive compound
1 day.....................	24.07% Cl or 5.1% of the additive compound
30 days....................	23.77% Cl or 7.6% of the additive compound

The toluides compared:

	Time.	% A. C.
ortho	months	43
meta	days	22
para	immediate	7

Propylamine.—An immediate flocculent precipitate[4] was formed. After three months it contained 25.67% Cl.

Calc. for $C_3H_7NH_2.HCl$: Cl, 37.09%.
Calc. for $C_6H_5SO_2.C_3H_7NH.HCl$: Cl, 15.04%. (A. C. 51.42%.)

Heptylamine.—Needles and leaflets[5] containing 15.53% Cl were formed at once. A second preparation yielded at once 17.10% Cl. A third preparation after one month yielded 23.10% Cl.

Calc. for $C_6H_5SO_2.C_7H_{15}NH.HCl$: Cl, 12.15%.
Calc. for $C_7H_{15}NH_2.HCl$: Cl, 23.37%. (A. C. 70, 56, 2.5%.)

Evidently the additive compound is decomposed by standing.

Benzidine.—A dark, flocculent precipitate was formed at once.

Calc. for $C_6H_5SO_2.NH.C_6H_4.C_6H_4NH_2.HCl$: Cl, 9.83%. Found: Cl, 8.73%.

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[1] $CH_3C_6H_4NH_2.HCl$, m. p. 215°. Ullmann, *Ber.*, **31**, 1699 (1898). Benzenesulfonyl-*o*-toluidide, m. p. 125–126°. Hinsberg, *Ann.*, **265**, 184 (1891); Bechmann and Fellrath, *Ibid.*, **273**, 13 (1893).

[2] $CH_3C_6H_4NH_2.HCl$, m. p. 228°. Ullmann, *Ber.*, **31**, 1699 (1898).

[3] $CH_3C_6H_4NH_2.HCl$, m. p. 238–240°. Bischoff and Walden, *Ann.*, **279**, 134 (1894). Krafft gives m. p. 236°. *Ber.*, **32**, 1601 (1899). Ullmann gives m. p. 243°. *Ibid.*, **31**, 1699 (1898). Benzenesulfonyl-*p*-toluidide melts at 120°. Wallach and Huth, *Ibid.*, **9**, 427 (1876). Rabout gives 122°. *Bull. soc. chem.*, [3] **15**, 1035 (1896).

[4] Propylamine hydrochloride melts at 158°. Topsöe, *Jahresber.*, **1883**, 621. $C_6H_5SO_2NH.C_3H_7$ melts at 36°. Solonina, *J. Russ. Phys. Chem. Soc.*, **29**, 404 (1897).

[5] $C_6H_5SO_2NH.C_7H_{15}$ is described as an oil solidifying at —20°. Solonina, *Loc. cit.;* Duden, *Ber.*, **33**, 478 (1900); Markwald, *Ibid.*, **32**, 3513 (1899).

Evidently the additive compound is contaminated with unchanged benzidine.

Phenylhydrazine.—A flocculent precipitate melting[1] at 202°.

Calc. for $C_6H_5SO_2.C_6H_5NH.NH.HCl$: Cl, 12.45%.
Calc. for $C_6H_5NH.NH_2.HCl$: Cl, 24.53%. Found: Cl, 15.63%. (A. C. 82%.)

Urea.—The solution remained clear in diffused sunlight and became clouded in direct sunlight. After months of standing prismatic needles softening at 70° and melting at 110–120°, were obtained.

Calc. for $C_6H_5SO_2Cl.CO(NH_2)_2$: Cl, 14.98%.
Calc. for $CO(NH_2)_2.HCl$: Cl, 36.72%. Found: Cl, 16.18%. (A. C. 94.4%.)

Secondary Bases.

Diethylamine.—Needles, softening at 130° and melting at 197°, were obtained. Two different preparations yielded 26.27% and 29.58% Cl.

Calc. for $C_6H_5SO_2.N(C_2H_5)_2.HCl$: Cl, 14.18%.
Calc. for $(C_2H_5)_2NH.HCl$: Cl, 32.30%. (A. C. 33.4 and 15.3%.)

Dipropylamine.—Leaflets containing 19.96% Cl were obtained.

Calc. for $C_6H_5SO_2N(C_3H_7)_2.HCl$: Cl, 12.76%.
Calc. for $(C_3H_7)_2NH.HCl$: Cl, 25.77%. (A. C. 45%.)

Diisobutylamine.—Large, thin, transparent, rhombic plates, softening at 127°, melting[2] at 145° and in two different preparations containing 18.14% and 18.95% Cl, were obtained.

Calc. for $C_6H_5SO_2.N(C_4H_9)_2.HCl$: Cl, 11.59%.
Calc. for $(C_4H_9)_2NH.HCl$: Cl, 21.4%. (A. C. 33 and 25%.)

Diisoamylamine.—Prisms, melting with decomposition at 205° and containing 17.63% Cl were obtained.

Calc. for $C_6H_5SO_2N(C_5H_{11})_2.HCl$: Cl, 10.62%.
Calc. for $(C_5H_{11})_2NH.HCl$: Cl, 18.31%. (A. C. 9%.)

Methylaniline.—Immediate cloudiness; crystals melting[3] at 154° and containing 24.03% Cl, were obtained.

Calc. for $C_6H_5SO_2.C_6H_5NCH_3.HCl$: Cl, 12.46%.
Calc. for $C_6H_5NCH_3.HCl$: Cl, 24.70%. (A. C. 5.47%.)

Ethylaniline.—The solution remained clear for hours. After eleven

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[1] Phenylhydrazine hydrochloride melts at 240°. Broche, *J. prakt. Chem.*, [2] **50**, 114 (1894). Authenreith gives 243–246°. *Ber.*, **29**, 1656 (1896). Benzenesulfonphenylhydrazide melts at 148–150°. Limpricht, *Ibid.*, **20**, 1239 (1887).

[2] $(C_5H_{11})_2NH.HCl$ melts at 288°. Hofmann, *Ann.*, **79**, 31 (1851). Malbot, *Ann. chim. phys.*, [6] **13**, 504 (1888); Berg, *Ibid.*, [7] **3**, 305 (1894); THIS JOURNAL, **34**, 1407 (1912). $C_6H_5SO_2N(C_5H_{11})_2$ melts at —20°. Solonina, *Loc. cit.*

[3] $C_6H_5NHCH_3.HCl$ melts at 121–122°. Scholl and Escales, *Ber.*, **30**, 3134 (1897); Menschutkin, *J. Russ. Phys. Chem. Soc.*, **30**, 252 (1898); THIS JOURNAL, **34**, 1406 (1912). $C_6H_5SO_2.C_6H_5NCH_3$ melts at 139°. Lellman, *Ber.*, **16**, 594 (1883); Brugnatelli, *Z. Kryst. Min.*, **30**, 191.

days large, glistening, hexagonal plates, softening at 125°, melting[1] at 174° and containing 21.05% Cl, were obtained.

Calc. for $C_6H_5SO_2.C_6H_5N.C_6H_5.HCl$: Cl, 11.90%.
Calc. for $C_6H_5NC_2H_5.HCl$: Cl, 22.49%. (A. C. 14.8%.)

Piperidine.—Immediate heavy, white, feathery masses of needles, melting[2] at 185° and containing in two different samples 25.33% Cl and 27.62% Cl. The former, after one year in a desiccator, yielded 21.57% Cl. Both dissolved in water with an acid reaction toward litmus.

Calc. for $C_6H_5SO_2.C_5H_{10}N.HCl$: Cl, 13.53%.
Calc. for $C_5H_{10}NH.HCl$: Cl, 29.17%. (A. C. 24.5 and 9.3%.)

Dibenzylamine.—Found: Cl, 13.17%. Calc. for $C_6H_5SO_2.N(C_7H_7)_2.HCl$: Cl, 9.47%. Calc. for $(C_7H_7)_2NH.HCl$: Cl, 15.18%. (A. C. 35%.)

Tertiary Bases.

Tribenzylamine.—A cloudiness resulted at once. After one week, microscopic prisms, melting[3] at 174–176°, were obtained.

Calc. for $(C_7H_7)_3N.C_6H_5SO_2Cl$: Cl, 7.64%.
Calc. for $[(C_7H_7)_3N]_2.C_6H_5SO_2Cl$: Cl, 4.72%. Found: Cl, 5.84 and 4.25%.

Evidently very nearly pure *di-tribenzylamine additive compound* was formed.

Tripropylamine.—The solution remained clear for two days. After two months, long, transparent needles, melting at 52°, were obtained. At first they gave 9.90% Cl; after recrystallizing from absolute alcohol, they gave 10.12% Cl.

Calc. for $(C_3H_7)_3N.C_6H_5SO_2Cl$: Cl, 11.08%.
Calc. for $[(C_3H_7)_3N]_2.C_6H_5SO_2Cl$: Cl, 7.66%.

Here *tripropylamine additive compound* was formed.

Triethylamine.—Short, hexagonal prisms, with pyramidal and truncated ends, also rhombic plates, were obtained. The mixture softened at 109–115° and melted[4] not sharply at 199°.

Calc. for $(C_2H_5)_3N.C_6H_5SO_2Cl$: Cl, 12.77%. Found: Cl, 15.76%.

Pyridine.—The crystals forming immediately were microscopic prisms. After a month large, transparent, rectangular plates, melting[5] not sharply at 84° and containing 8.24% Cl, were obtained. After recrystallizing from alcohol, that melted at 110–112° and contained 13.34% Cl.

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[1] $C_6H_5NHC_2H_5.HCl$ melts at 172–175°. Reynolds, *J. Chem. Soc.*, **61**, 455 (1892). Bischoff gives 176°. *Ber.*, **30**, 3178 (1897). $C_6H_5SO_2.C_6H_5NC_2H_5$ melts at 87–88°. Brugnatelli and Otto, *J. prakt. Chem.*, [2] **47**, 372 (1893); *Z. Kryst. Min.*, **30**, 191.

[2] $C_5H_{10}NH.HCl$ melts at 237°. Ladenburg, *Ann.*, **247**, 55 (1888). Colson describes a dihydrochloride. *Compt. rend.*, **124**, 504 (1897); **132**, 1563 (1901). $C_6H_5SO_2.C_5H_{10}N$ melts at 93–94°. Hindberg, *Ann.*, **265**, 182 (1891); Schlömann, *Ber.*, **24**, 3689 (1891).

[3] Tribenzylamine hydrochloride melts at 227–228°. Spica, *Atti istit. ven.*, [5] **7**.

[4] Triethylamine hydrochloride melts at 256°.

[5] Pyridine hydrochloride forms needles and melts at 128°.

Calc. for $(C_5H_5N)_2.C_6H_5SO_2Cl$: Cl, 8.56%.
Calc. for $C_5H_5N.C_6H_5SO_2Cl$: Cl, 13.85%.

Evidently *two different additive*[1] *compounds* were present here.

α-Picoline.—After months, needles and an oil were obtained. Crystals obtained by cooling at 4°, contained 9.23% Cl.

Calc. for $(C_6H_7N)_2.C_6H_5SO_2Cl$: Cl, 9.79%.

A *dipicoline additive compound* was formed.

Quinoline.—Needles were first formed, then thick, rhombic plates and prisms. The crystalline masses melted[2] at 70–79°. After two days they contained 10.05% Cl. After three months, they contained 8.36% Cl.

Calc. for $C_9H_7N.C_6H_5SO_2Cl$: Cl, 11.58%.
Calc. for $(C_9H_7N)_2.C_6H_5SO_2Cl$: Cl, 8.19%.

Evidently first the *mono-*, then the *diquinoline additive compound* is formed.

Quinaldine.—After three months, tufts of microscopic needles and prisms, melting at 140° and containing 9.61% Cl were obtained. After recrystallizing from absolute alcohol, the substance melted at 150° and contained 9.75% Cl.

Calc. for $C_{10}H_9N.C_6H_5SO_2Cl$: Cl, 11.08%.
Calc. for $(C_{10}H_9N)_2.C_6H_6SO_2Cl$: Cl, 7.66%.

Here a mixture of the *mono-* and the *diquinaldine additive compounds* were formed.

Acridine.—Golden, prismatic needles, softening at 165° and melting at 192°, were obtained.

Calc. for $(C_{13}H_9N)_2.C_6H_6SO_2Cl$: Cl, 6.63%. Found: Cl, 6.26 and 7.26%.

The *diacridine additive compound* was formed.

Antipyrine.—Needles, containing 14.19% Cl, were obtained.

Calc. for $C_6H_5SO_2Cl.C_{11}H_{12}N_2O$: Cl, 9.48%.
Calc. for $(C_6H_5SO_2Cl)_2.C_{11}H_{12}N_2O$: Cl, 13.09%.

Evidently the *additive compound* contains one molecule of antipyrine and two molecules of benzenesulfonylchloride.

Summary.

1. Benzenesulfonylchloride reacts in anhydrous ether with primary, secondary and tertiary bases. The initial products formed in all cases are additive. Owing to varying conditions of moisture and temperature, dissociated products are obtained. With the original materials, these may yield secondary products which often are present with the additive products.

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[1] For the analogous additive compounds of pyridine with inorganic halides, see the Beilstein.

[2] Quinoline hydrochloride melts at 94°. deConinck, *Ann. chim. phys.*, [5] **27**, 488 (1882).

2. Tertiary compounds add one or two molecules of the base to one molecule of the benzenesulfonylchloride.
3. Light promotes all of these reactions.
4. The reactions are non-ionic.

SEATTLE, WASH.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF YALE UNIVERSITY.]

THE RELATIVE STABILITY OF HALOGEN SUBSTITUTED ALIPHATIC ACIDS IN WATER SOLUTION.

BY W. A. DRUSHEL AND G. S. SIMPSON.

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Among the investigators who have studied the stability of a few of the halogen substituted acids under various conditions are Buchanan,[1] Schwab,[2] Wislicenus,[3] Kastle,[4] DeBarr,[5] Bischoff,[6] Lossen,[7] Slator,[8] Bevan,[9] Senter,[10] Euler,[11] Clark,[12] Madsen,[13] and Johanssen.[14] In general the method of investigation has been to determine the rate of replacement of the halogen atom by certain groups. Since hydrolysis offers a method which is easy in manipulation and which is not complicated by side reactions it has been used by several investigators of this problem. This reaction in which the halogen atom is replaced by the hydroxyl group has been called hydroxylation by Frankland.[15]

The most extensive work in this field has been done by DeBarr and by Senter. DeBarr has shown that many of these compounds are very stable toward water at the ordinary temperatures. In his experiments he found that secondary reactions accompanied the hydrolysis of several α-, β-, and γ-halogen substituted acids at 150°. Senter has conducted a series of important experiments in which he has studied the mechanism of the hydrolysis of the substituted aliphatic acids. Most of his work has been done on the α-brom substituted acids or their salts. He has shown that halogen acids act as negative catalysts. By means of a derived equation

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[1] *Ber.*, **4**, 863 (1871).

[2] *Etades de Dyn. Chem.*, **1884**, 20.

[3] *Ann.*, **212**, 239 (1882).

[4] *Am. Chem. J.*, **14**, 586 (1892); **15**, 471 (1893).

[5] *Ibid.*, **22**, 333 (1899).

[6] *Ber.*, **32**, 1748 (1899).

[7] *Ann.*, **342**, 112 (1905).

[8] *Trans. Chem. Soc.*, **87**, 482 (1905); **95**, 93 (1909).

[9] *Proc. Camb. Phil. Soc.*, **13**, 269 (1906).

[10] *Trans. Chem. Soc.*, **91**, 466 (1907); **95**, 1827 (1909); **99**, 1049 (1911).

[11] *Ber.*, **39**, 2726 (1906).

[12] *Trans. Chem. Soc.*, **97**, 416 (1910).

[13] *Ibid.*, **103**, 965 (1913).

[14] *Ber.*, **48**, 1262 (1915).

[15] *Trans. Chem. Soc.*, **103**, 713 (1913).