The ionization constant of the base, K_b, may be computed from the well-known expression, $K_b = K_w/K_h$, whence we obtain $K_b = 1.02 \times 10^{-14}/2.53 \times 10^{-6} = 4.03 \times 10^{-9}$. This value is in harmony with the work of Stieglitz and his associates on related compounds.

Summary

γ-Chloropropyl imidobenzoate hydrochloride has been synthesized in order to compare its stability in water with that of the propyl compound studied by Stieglitz. The value of 0.00784 for the reaction velocity constant of our compound at 25° shows that γ-chlorosubstitution in the propyl group has an accelerating effect on the saponification of the imino group. The affinity constant of the base has also been ascertained. Work on a number of related compounds will be reported later.

TROY, N. Y. RECEIVED OCTOBER 13, 1937

Alkylation of Reactive Methylene Groups with Alkyl Sulfates

BY EVERETT BOWDEN

The alkylation of compounds containing reactive methylene groups has almost always been carried out using alkyl halides; alkylations by methyl and ethyl sulfate have been very largely confined to phenols, amines, and acids. The practicability of effecting carbon to carbon alkylations by alkyl sulfates seems to have been largely overlooked. Thus, of the compounds mentioned below only benzoylacetone[1] and malonic ester[2] seem to have been alkylated by alkyl sulfates, and the yields were not reported. We have carried out a series of carbon to carbon alkylations and the results indicate that these reactions can be effected as satisfactorily with alkyl sulfates as with alkyl halides, and cheaper. (The higher boiling point of the alkyl sulfates is also advantageous, since it permits a higher reaction temperature.) Acetoacetic ester, camphor and cyanacetic ester were alkylated to the corresponding monoethyl derivative with yields of 87, 45, and 75% as compared to yields of 82,[3] 50,[4] and 74%[5] as reported in the literature.

Malonic ester was methylated in alcohol using sodium ethoxide and methyl sulfate. Malonic ester, acetoacetic ester, ethyl acetoacetic ester, benzoylacetone and cyanoacetic ester (two alkylations, mono- and dialkylated) were ethylated by diethyl sulfate and sodium ethoxide in alcohol. Phenylacetic ester was alkylated by ethyl sulfate using sodium in ether. Benzyl cyanide, butyl cyanide, acetophenone, isobutyl methyl ketone and camphor were alkylated using diethyl sulfate and sodamide in an inert solvent. For the sake of brevity only two preparations are described in this paper.

Alkylation of Benzyl Cyanide.—Eleven grams of sodamide was suspended in 125 ml. of dry ether. Twenty-nine grams of benzyl cyanide was added over a period of one hour. Ammonia was evolved and the mixture boiled gently under reflux. The flask was warmed for another fifteen minutes, then 38 g. (0.25 mole) of diethyl sulfate added drop by drop, each addition producing a violent reaction. The addition required one-half to three-quarters of an hour. Cooling was required and much ammonia was evolved. Fifty ml. of dry ether was added to the heavy sludge, and the mass allowed to stand overnight. Most of the ether was then distilled with stirring, the residue was dissolved in water, the oil separated and the aqueous layer extracted twice with ether. The combined oil and ether were washed once with water and fractionated: yield 33 g., b. p. 105–106° at 8 mm. (89% of calcd.) of α-phenylbutyronitrile.

Preparation of Diethyl Acetonitrile.—Eighty-one grams (1.00 mole) of ethyl cyanoacetate was dissolved in an equal volume of very dry ethanol; then 154 g. (1.00 mole) of diethyl sulfate was added. This was followed in the cold by 46 g. (2.00 mole) of sodium dissolved in 400 ml. of absolute alcohol. Another mole of diethyl sulfate was then added in portions.

The contents of the flask were next subjected to slow distillation, the last of the alcohol being removed *in vacuo*. The residue was dissolved as well as possible in a small quantity of water, the mixture stirred in the cold one to two hours, while a cold concentrated solution of 55 g. of sodium hydroxide in water was slowly dropped in, the volume of the mixture being maintained at 200–300 ml. When solution was practically complete, the mixture was extracted with benzene, acidified with excess hydrochloric acid, again extracted thoroughly with benzene. This benzene was distilled and the oily residue decarboxylated in the same apparatus, followed by fractionation: yield 60 g.; b. p. 142–146° (60% of the theoretical, over the entire reaction).

Conclusion

Alkylation of various representative compounds containing reactive methylene groups has been carried out satisfactorily using methyl and ethyl sulfates.

MADISON, WIS. RECEIVED NOVEMBER 22, 1937

---

(1) Auwers, *Ber.*, **45**, 996 (1912).

(2) Nef, *Ann.*, **309**, 188 (1899).

(3) Conrad-Limpach, *ibid.*, **192**, 155 (1878).

(4) Haller and Louvier, *Ann. chim.*, [9] **9**, 190 (1918).

(5) Hessler, *Am. Chem. J.*, **22**, 170 (1899).