fractionated. A yield of 68.5 g. (90%) of trifluoroisopropanol (b. p. 77–78°) was obtained.

CHEMICAL LABORATORY
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RECEIVED[6] MAY 6, 1943

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[6] This manuscript was originally received on May 6, 1943, and after examination was accepted for publication in the Journal. It was, however, referred to the National Defense Research Committee, and at their request was withheld from publication, in a confidential file, until it was finally cleared for publication on January 14, 1946.

Preparation of Schiff Bases by Condensation of 2-Acylthiophenes with Amines

BY HOWARD D. HARTOUGH

In contrast to the circuitous procedure involved in the preparation of Schiff bases from acetophenone,[1] 2-acetylthiophene condenses directly with aniline and primary aliphatic amines, without the aid of a catalyst, in boiling toluene or xylene. 2-Butanoylthiophene condenses very slowly with aniline and the reaction apparently can be catalyzed by addition of iodine. Zinc chloride could not be used to catalyze this reaction since an insoluble complex formed with the 2-acylthiophenes. Although the best yields obtained were not greater than 46%, the original reactants could be completely recovered and the product distilled without loss due to high boiling residues.

These ketimines are readily hydrolyzed with moisture to the original components. A loosely stoppered bottle of pure crystalline N-phenyl 2-thienyl methyl ketimine stored in a humid atmosphere became semi-crystalline at the top of the bottle and the odor of 2-acetylthiophene was prevalent.

Experimental

N-Phenyl 2-Thienyl Methyl Ketimine.—A mixture of 0.5 mole each of aniline and 2-acetylthiophene was heated at reflux in 150 ml. of toluene in a flask to which was attached a conventional water take-off trap and a reflux condenser. After thirteen hours, 5 ml. of water (9 ml. calcd.) was collected in the trap. Heating at reflux an additional six hours did not increase the amount of water. The toluene was recovered by distillation at atmospheric pressure; the aniline and 2-acetylthiophene at a reduced pressure. The bright yellow product, 45 g. (46%), boiling at 155° at 5 mm. crystallized on standing and after one recrystallization from absolute alcohol melted at 69–70°.

Anal. Calcd. for $C_{12}H_{11}NS$: N, 7.0; S, 16.0. Found: N, 7.1; S, 16.1.

N-(2-Ethylhexyl) 2-Thienyl Methyl Ketimine.—An equimolar mixture (0.325 mole) of 2-acetylthiophene and 2-ethylhexylamine in 500 ml. of toluene was refluxed for twenty-two hours as above. The liquid product, 30 g. (40%), boiled at 150–157° at 4 mm.

Anal. Calcd. for $C_{14}H_{23}NS$: N, 5.91. Found: N, 6.07.

N-Phenyl 2-Thienyl Propyl Ketimine.—A mixture of 2-butanoylthiophene (0.25 mole) and aniline (0.50 mole) in 500 ml. of toluene was refluxed for four hours, but only 0.3 ml. of water was collected. The mixture was cooled, 3 g. of iodine added, and refluxed five hours more, 1.0 ml. of water being collected. The liquid product, 16 g. (28%), boiled at 128–130° at 1 mm.

Anal. Calcd. for $C_{14}H_{15}NS$: N, 6.12. Found: N, 6.19.

SOCONY-VACUUM LABORATORIES
(A DIVISION OF THE SOCONY-VACUUM OIL CO., INC.)
RESEARCH AND DEVELOPMENT DIVISION
PAULSBORO, N. J.
RECEIVED DECEMBER 15, 1947

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[1] Claisen, *Ber.*, **29**, 2932 (1896), describes the preparation of these bases from acetophenone by condensation of amines with ketals of acetophenone.

Low Temperature Nitrogen Adsorption Studies of Silica Gel

BY ISIDOR KIRSHENBAUM AND RICHARD K. GROVER

Recently a number of papers have appeared upon the effect of sintering *in vacuo* and of grinding upon the surface area and average pore size of gel type materials. Milligan and Rachford[1] have reported that sintering a silica gel causes destruction of pores but no change in average pore size. Van Nordstrand, Kreger and Ries[2] have found that grinding Thermofor Catalytic Cracking beads to a fine powder results in a considerable decrease in both surface area and pore volume. Apparently, however, this latter phenomenon is not restricted to silica–alumina cracking catalysts. Similar observations have recently been made in our laboratories, using a Davison silica gel, activated at 650° and having a surface area of 655 sq. m./g. Upon grinding from 80+ microns to a powder containing about 40% 0–80 micron and 60% 80+ micron particles, the surface area was decreased by 8.6% to 599 sq. m./g. Typical data are summarized in Table I. Both ground and unground samples were evacuated for four hours at 290° before the nitrogen adsorption isotherms were obtained, previous work having indicated that this pretreatment is sufficient to give results reproducible to better than about 1%. The changes observed upon grinding may be due to a partial collapse of pore structure effected by the heat and/or pressure of grinding.

TABLE I

EFFECT OF GRINDING ON ACTIVATED SILICA GEL

Sample	Roller analysis Microns	%	Weight loss on evacuation, %	Surface area sq. m./g.
Unground	0–20	2.8	5	655
	20–40	1.7		
	40–80	1.7		
	80+	93.8		
Ground	0–20	14.7	5	599
	20–40	10.3		
	40–80	13.7		
	80+	60.9		

This effect of grinding was also observed with a silica gel containing about 64% water. A sample of the gel was ground and then both ground and

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[1] Milligan and Rachford, *J. Phys. Colloid Chem.*, **51**, 333 (1947).

[2] R. A. Van Nordstrand, W. E. Kreger and H. E. Ries, Jr., A. C. S. Meeting, Divn. of Petrol. Chem., New York City, September, 1947.

unground samples were evacuated at 290° for four hours. The surface area of the unground catalyst, as determined from the nitrogen adsorption isotherm, using the weight after evacuation, was 1061 sq. m./g., whereas that of the ground catalyst was 991 sq. m./g., a difference of 6.7%. Little, if any, effect was observed on the average Kelvin pore radius, as determined from the relative pressure corresponding to the steepest portion of the desorption curve. The unground sample had an average pore size of 21.1 A., whereas the ground sample had an average pore radius of 20.7Å.

STANDARD OIL DEVELOPMENT CO.
ELIZABETH, NEW JERSEY
RECEIVED DECEMBER 4, 1947

Preparation and Characterization of β-Dibutylaminoethyl Chloride Hydrochloride

BY HOWARD C. KLEIN[1] AND IRVING A. KAYE

β-Dibutylaminoethyl chloride hydrochloride has been prepared by the dropwise addition of 47.2 g. (0.4 mole) of thionyl chloride to 51.9 g. (0.3 mole) of β-dibutylaminoethanol, dissolved in 150 ml. of benzene. After removal of the solvent and excess thionyl chloride under diminished pressure, the tarry residue was dissolved in dry acetone, the solution decolorized with Darco G-60, and then cooled with Dry Ice. The precipitated white hydrochloride (57.9 g., 85%) melted at 86–88°.

Anal. Calcd. for $C_{10}H_{23}NCl_2$: Cl^-, 15.41; Cl (total), 30.82. Found: Cl^-, 15.30; Cl (total), 30.92.

Recrystallization of the hydrochloride from acetone–hexane gave pearly leaflets, m.p. 87–89°.

The basic chloride boiled at 119–120° (30 mm.).[2]

(1) Nopco Chemical Company, Fine Chemicals Division, Harrison, New Jersey.

(2) Blicke and Maxwell, THIS JOURNAL, **64**, 429 (1942), found 114–115° (23 mm.).

DEPARTMENT OF CHEMISTRY
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RECEIVED NOVEMBER 10, 1947

Synthesis of Amino-substituted Phosphonic Acids. II. α-Aminobenzylphosphonic Acid

BY GENNADY M. KOSOLAPOFF

As it was reported earlier[1] the synthesis of α-aminobenzylphosphonic acid by the reduction of *p*-nitrophenylhydrazone of diethyl benzoylphosphonate by means of hydrogen, followed by sodium sulfide, failed to yield the pure product. The contamination of the final product was caused principally by the products of incomplete reduction and led to the unusually low melting point of the substance. In order to secure the pure material it was necessary to find another reduction method which was usable in this instance. Such a procedure using the method of Fischer and Groh[2] for the reduction led to the pure substance.

The hydrazone (4 g.) in 500 cc. of ethanol was added to 10 g. of amalgamated aluminum foil immersed in 1 liter of ethanol and 200 cc. of water. The mixture was allowed to stand overnight in a loosely stoppered flask. After filtration, the precipitate was washed with 500 cc. of ethanol and the combined filtrates were treated with 300 cc. of concentrated hydrochloric acid. The solution was slowly distilled (six hours) through a Vigreux column until the volume in the still-pot amounted to approximately 50 cc. On cooling, the *p*-phenylenediamine hydrochloride was filtered off, the filtrate was evaporated to dryness by an infrared lamp and the residue was taken up in 200 cc. of ethanol. Neutralization with aniline gave the crude product which was taken up in 30 cc. of warm water, made strongly alkaline with 10% sodium hydroxide and extracted twice with 50 cc. of benzene. The aqueous solution was made just acid to congo red with 1:1 hydrochloric acid and concentrated to incipient crystallization. After cooling, the product was filtered off, washed with 5 cc. of ice-water, dissolved in 50 cc. of hot water, treated with charcoal, filtered and concentrated to 10 cc. On cooling there was obtained 1.0 g. (50%) of *dl*-α-aminobenzylphosphonic acid, in the form of tiny bunched colorless needles, which melted at 272–273°.

Anal. Calcd.: N, 7.5; P, 16.6. Found: N, 7.46; P, 16.7.

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(1) Kosolapoff, THIS JOURNAL, **69**, 2112 (1947).

(2) Fischer and Groh, *Ann.*, **383**, 363 (1911).

CENTRAL RESEARCH DEPARTMENT
MONSANTO CHEMICAL COMPANY
DAYTON 7, OHIO
RECEIVED SEPTEMBER 27, 1947

Copolymerization Rate Constants in the System 2,5-Dichlorostyrene–Methyl Acrylate

BY F. LEONARD, W. P. HOHENSTEIN AND E. MERZ

During the course of an investigation of the copolymerization of the isomeric dichlorostyrenes and acrylic esters, it became of interest to determine the copolymerization rate constants in the system 2,5-dichlorostyrene and methyl acrylate. The results of this determination are herein presented.

Experimental

2,5-Dichlorostyrene.—This monomer was obtained from the Monsanto Chemical Co. and was purified by washing with 5% sodium hydroxide solution and then with distilled water until the washes were neutral to litmus. The monomer was allowed to dry over calcium chloride overnight. It was then filtered and checked for the presence of polymer by adding a sample to methanol. If no turbidity was observed, the monomer was used *per se*.

Methyl Acrylate.—This monomer obtained from Rohm and Haas was distilled *in vacuo* through a 12″ column packed with glass helices in an all-glass system. The first 10 cc. to distil was rejected and a residue of 50 cc. was left in the distilling flask.

Polymerization and Purification.—The requisite quantities of 2,5-dichlorostyrene, methyl acrylate and benzoyl peroxide (0.5% by weight based on monomers) were weighed into Pyrex glass test-tubes. The tubes were sealed, and immersed in a water-bath held at 70 ± 0.1°. The per cent. conversion was estimated approximately by the rate of rise of air bubbles through the polymerizing mixture when the tubes were inverted. When it appeared that the desired conversion, <5%, had been reached, the tubes were immediately chilled, and the