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

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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.

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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.