The potassium salt used was then added and methanol was distilled off with stirring to obtain a uniform dispersion. Complete removal of methanol was effected by applying reduced pressure (20–30 mm.) and the resulting solid was heated in a solder-bath between 300 and 350°. The reaction occurs at the internal temperature of 300–310° as evidenced by rapid distillation of toluidine. Reduced pressure (20–30 mm.) was applied toward the end of the reaction to remove all toluidine. The reaction mass was cooled, treated with water and the indole steam-distilled over. The product crystallized in the cooled distillate in the form of lustrous plates. Any trace of toluidine was removed by acidification and the indole was filtered, washed with water and dried; m. p. 50–51.5°.

Since half of the toluidine was recovered in every case, the yield was calculated on the basis of this recovery. The results obtained are contained in Table I.

TABLE I

g.	Added salt,	K atoms	Yield, %	Observations
None		..	6.0	
17	Anhydrous K_2SO_4	1	14.5	No stirring used; melt appears heterogeneous
35	Anhydrous K_2SO_4	2	21.0	
70	Anhydrous K_2SO_4	4	14.5	
35	Anhydrous K_2SO_4	2	34.0	Mechanical stirring used
20	Anhydrous KOAc	1	27.0	Homogeneous fluid melt
39	Anhydrous KOAc	2	37.5	

Whether the potassium acts as a catalyst or as a reactant is open to question. The data show that a potassium salt does effect a marked increase in yield, the maximum effect being obtained apparently with two atoms of potassium.

Although the yield is not as high as when potassium metal is used, the procedure is safer and much less expensive.

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The Preparation of 2,2,2-Trifluoroethanol

BY HENRY GILMAN AND R. G. JONES

In connection with studies of compounds containing the trifluoromethyl group, we had need of trifluoroethanol. This substance had been described by Swarts[1] who prepared it by the catalytic reduction both of trifluoroacetic anhydride and of trifluoroacetamide. Since the former method afforded him a yield of only 23%, we attempted in vain its preparation from both ethyl and *n*-butyl trifluoroacetate by hydrogenation over copper chromite catalyst at pressures up to 3500 lb./sq. in. and temperatures up to 250°. No hydrogen was absorbed and we recovered unchanged 70% of the ethyl, and 32% of the butyl ester.

In view of this failure we resorted to the latter method of Swarts, who unfortunately gave no details of his procedure other than that he hydrogenated the ethereal solution under a pressure of 40 atmospheres.

Trifluoroethanol.—A solution of 113 g. (1.0 mole) of pure amide (m. p. 74.5–75.0°) in 100 cc. of anhydrous ether in a bomb of 490-cc. capacity with 3.5 g. of Adams catalyst was agitated with hydrogen at 1500 lb./sq. in. at 90° for seven hours, the pressure dropping to 670 lb./sq. in. To the cooled bomb 1.5 g. of fresh catalyst was added and agitation at the previous temperature and pressure was continued for four hours longer, the pressure then dropping to 1080 lb./sq. in. The contents of the cooled bomb with the ether washings was fractionated in a small packed column of about 10 equivalent plates, yielding a fraction weighing 76.5 g. (76.5%) and boiling at 75–77° (740 mm.). It was necessary to heat the distilling flask with a free flame in order to drive over the trifluoroethanol. Apparently the latter forms an unusually stable solvate with the unchanged trifluoroacetamide and ammonium trifluoroacetate present. The released hydrogen in each case was allowed to bubble through concentrated hydrochloric acid, whereby a total of 36 g. of ammonium chloride (66% yield), identified by analysis, was obtained.

The platinum catalyst seemed to quickly lose its activity. In all of the runs the rate of reduction became very slow after about four hours and it was necessary to add fresh catalyst.

From several preparations, the general reaction for which may be represented as

$$CF_3CONH_2 + 2H_2 \xrightarrow{Pt} CF_3CH_2OH + NH_3$$

none of the recently described[2] trifluoroethylamine was isolated. The only products were trifluoroethanol, ammonia, unchanged trifluoroacetamide, and ammonium trifluoroacetate. The small quantity of ammonium trifluoroacetate obtained may have resulted from hydrolysis of trifluoroacetamide.[3]

Trifluoroisopropanol.[4]—Seventy-five grams (0.67 mole) of trifluoroacetone,[5] 5 g. of Adams catalyst, and 3 cc. of water, were added to the bomb previously cooled to −15°, and the whole agitated at room temperature with hydrogen at 760 lb./sq. in. pressure. The absorption of hydrogen began at once and in three hours the pressure had dropped to 250 lb./sq. in. The bomb was then opened and the contents and ether washings were dried over calcium sulfate and

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[1] Swarts, *Compt. rend.*, **197**, 1261 (1933); *Bull. soc. chim. Belg.*, **43**, 471 (1934) [*C. A.*, **29**, 729 (1935)].

[2] Gilman and Jones, THIS JOURNAL, **65**, 1458 (1943).

[3] Although care was taken to dry the reagents and the apparatus, sufficient water may have been formed from the catalyst [$PtO_2 \cdot H_2O$].

[4] Swarts, *Bull. soc. chim. Belg.*, **38**, 99 (1929) [*C. A.*, **23**, 4440 (1929)].

[5] Swarts, *Bull. classe. sci. Acad. roy. Belg.*, **13**, 175 (1927). [*C. A.*, **22**, 58 (1928)].

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

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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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[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.