driving force for ring expansion even in the presence of the electronegative groups.

Treatment of the amine, I, with nitrous acid under modified Demjanow conditions[6] resulted in a 69% yield of an alcohol fraction and <5% unidentified olefins. A small amount of the starting amine was recovered as the benzamide. The alcohol fraction was identified as consisting of >95% unrearranged alcohol, 2,2,3,3-tetrafluorocyclobutanemethanol, II. None of the expected ring-enlarged product, tetrafluorocyclopentanol, was obtained. The alcohol fraction was identified by NMR and comparison of the physical properties and derivatives with those of an authentic sample of II, prepared by the cyclodimerization of tetrafluoroethylene and allyl alcohol.[7]

This is the first example in which a simple cyclobutanemethylamine has failed to show ring enlargement on deamination.

EXPERIMENTAL

2,2,3,3-Tetrafluorocyclobutanecarbonitrile. This compound was prepared according to the method of Coffman[7] from acrylonitrile and tetrafluoroethylene. The fraction having a b.p. 72–73.5° (50 mm.) was collected.

2,2,3,3-Tetrafluorocyclobutanemethylamine, I. A mixture of tetrafluorocyclobutanecarbonitrile (46.8 g., 0.3 mole), acetic anhydride (33 g., 0.33 mole), anhydrous ethyl ether (90 ml.), and PtO₂ (2.0 g.) was placed in a hydrogenation bomb. The bomb was pressured to 1000 p.s.i.g. with hydrogen and the temperature was slowly raised while agitating. At 60°, the pressure dropped to 500 p.s.i.g. in 10 min. The bomb was repressured to 1000 p.s.i.g. and held for 2 hr. at 60°. The final pressure was 850 p.s.i.g. The cooled reaction products were filtered to remove the catalyst and the excess ether and acetic anhydride were removed under vacuum to yield a viscous oil (62.3 g.). The oily product, believed to be an acetyl derivative, was refluxed for 6 hr. in 30% sulfuric acid. The hydrolysis mass was cooled and made slightly alkaline with sodium hydroxide and extracted with three 100-ml. portions of ether. The combined ether portion was dried over potassium hydroxide pellets. Some decomposition occurred in the drying step as evidenced by considerable darkening of the ether solution. The ether solution was decanted from the potassium hydroxide and distilled through a 36-in. spinning band column. The amine, b.p. 43–45° (20 mm.), was isolated as a colorless oil in a 30% over-all yield from the nitrile.

Anal. Calcd. for C₅H₅F₄N: C, 38.3: H, 4.46; N, 8.9. Found: C, 38.3; H, 4.85; N, 8.7.

The benzamide was prepared and formed white plates from aqueous ethanol, m.p. 92.0–92.5°.

Anal. Calcd. for C₁₂H₁₁F₄NO: C, 55.1; H, 4.2; N, 5.4. Found: C, 55.7; H, 4.3; N, 5.6.

Deamination of I. To a solution of I (10.0 g., 0.064 mole) and monobasic sodium phosphate (35 g., 0.25 mole) in 150 ml. water was added a solution of sodium nitrite (4.5 g., 0.065 mole) in 10 ml. of water. The resulting mixture was heated at reflux for 4 hr. Nitrogen was evolved and a brown oil formed on the surface. The oil layer was extracted with three 30-ml. portions of ether; the ether portions were combined, dried, and distilled. A small forerun, b.p. 87–153°, was obtained and the main fraction, 5.8 g., distilled at 153–

155°. Some decomposition occurred in the pot and the residue amounted to 1.1 g. A small amount of unreacted amine (0.2 g.) was recovered from the aqueous solution as the benzamide. The p-nitrobenzoate of the alcohol fraction was prepared and formed white needles from aqueous ethanol, m.p. 90–91°.

Anal. Calcd. for C₁₂H₉F₄NO₄: C, 47.0; H, 2.9. Found: C, 47.3; H, 3.0.

An authentic sample of 2,2,3,3-tetrafluorocyclobutanemethanol was prepared according to the method of Coffman,[7] from tetrafluoroethylene and allyl alcohol. The product, b.p. 155–156° (760 mm.), had an identical infrared spectrum with the deaminated product from I with the exception of a minor band at 5.95 microns. This band could be due either to carbonyl or an unsaturated fluorine compound present to a small extent in the deaminated product.

The p-nitrobenzoate of the known alcohol melted at 90–91° and showed no depression on admixture with the derivative of the deaminated product.

RESEARCH DIVISION CONTRIBUTION No. 268
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Reduction of Carbonyl Compounds with Pyridine Borane

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The reduction of various carbonyl compounds with pyridine borane to the alcohol stage has been studied qualitatively. This reagent reduces aldehydes and ketones (chiefly aromatic) in yields ranging from 24% to 94%; acids and acid chlorides in yields ranging from 21% to 40%. All attempts to reduce esters and salts of carboxylic acids failed.

The reduction of carbonyl compounds with various hydrides has been the subject of several investigations.[2–4] Such an investigation has been carried out in this laboratory with pyridine borane, one of the several known borine complexes.

Pyridine borane was first prepared by Schlesinger and co-workers,[5] by the reaction of diborane and pyridine using vacuum techniques. A more convenient synthesis was developed by Taylor and associates,[6] using anhydrous pyridine hydrochloride and sodium borohydride in pyridine as the solvent.

(1) In partial fulfillment of the requirements for the master's degree.

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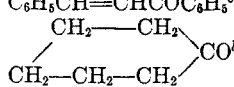(3) R. F. Nystrom, S. W. Chaiken, and W. G. Brown, *J. Am. Chem. Soc.,* **71**, 3245 (1949).

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Carbonyl Compound	Moles of Carbonyl Compound	Moles of Reagent	Volume of Solvent	Refluxing Time	% Reduction
$C_6H_5CHO^a$	0.180	0.065	50 Cc. ether	3 Hr.	0.0
$C_6H_5CHO^b$	0.190	0.067	40 Cc. benzene	4 Hr.	24.0
C_6H_5CHO	0.190	0.150	f	5 Min.	57.5
p-$BrC_6H_4CHO^a$	0.058	0.019	30 Cc. isopropyl ether	45 Min.	94.0
p-$BrC_6H_4CHO^b$	0.810	0.030	25 Cc. benzene	1 Hr.	74.0
p-NO_2—$C_6H_4CHO^b$	0.033	0.012	40 Cc. benzene	30 Min.	76.0
p-Cl—$C_6H_4CHO^b$	0.072	0.028	25 Cc. toluene	1.25 Hr.	74.0
$C_6H_5CH{=}CH$—CHO^a	0.114	0.040	30 Cc. isoamyl ether	1 Hr.	0.0
$C_6H_5CH{=}CH$—CHO^b	0.055	0.055	15 Cc. benzene	1.5 Hr.	84.0
p-CH_3O—$C_6H_4CHO^a$	0.147	0.054	25 Cc. benzene	2 Hr.	0.0
p-CH_3O—C_6H_4—CHO^b	0.023	0.060	5 Cc. benzene	2 Hr.	0.0
o-$HOC_6H_4CHO^b$	0.148	0.101	20 Cc. benzene	7 Hr.	0.0
$C_6H_5CH{=}CH$—$COC_6H_5^a$	0.048	0.016	35 Cc. isoamyl ether	20 Min.	0.0
$C_6H_5CH{=}CH$—$COC_6H_5^a$	0.072	0.025	25 Cc. n-butyl ether	18 Hr.	0.0
$C_6H_5CH{=}CHCOC_6H_5^b$	0.054	0.054	30 Cc. toluene	4 Hr.	84.0
CH_2——CH_2 ⟍CO^b / CH_2—CH_2—CH_2 ⟋	0.240	0.088^c	15 Cc. benzene	2.5 Hr.	25.0
$C_6H_5COC_6H_5^b$	0.066	0.066 ·	20 Cc. toluene	5 Hr.	83.0
$C_6H_5CO_2H^a$	0.041	0.041	15 Cc. n-butyl ether	2.5 Hr.	27.6
n-$C_{17}H_{35}CO_2H^b$	0.035	0.036	30 Cc. toluene	4 Hr.	40.0
$C_6H_5COCl^b$	0.049	0.049	25 Cc. carbon tetrachloride	30 Min.	21.1
n-$C_3H_7COCl^b$	0.123	0.096	50 Cc. chloroform	3.5 Hr.	27.0
Salts^{a,d}	—	—	—	3.5 Hr.	0.0
Esters^{b,e}	—	—	f	3.5 Hr.	0.0

[a] Procedure I. [b] Procedure II. [c] The reagent used here was gamma-picoline borane, a white solid, m.p., 72°, prepared similarly to pyridine borane. [d] Potassium benzoate in aqueous methanol and potassium p-bromobenzoate in benzene. [e] Ethyl benzoate, n-butyl stearate, n-propylphenyl acetate, and ethyl p-chlorobenzoate. [f] No solvent was used.

It is a pale yellow, practically odorless liquid which is stable in air, insoluble in and only slightly hydrolyzed by water, and very soluble in the common organic solvents. It melts at 11°, and according to Burg,[7] exhibits an equilibrium vapor pressure of 1.8 mm. at 100° without dissociation.

The results of this study clearly indicates that the reducing power of pyridine borane is considerably less than that of those hydrides heretofore used for this purpose.

This choice of solvent, primarily as regards its boiling point, appears to have a definite effect on the success of the reduction. Little or no reaction occurs with aldehydes or ketones in low boiling solvents such as ethyl ether, and polymerization takes place readily in high boiling solvents such as isoamyl ether. The tendency toward polymerization is greater in reactions with ketones than with aldehydes even in solvents of moderate boiling point. It was found that the best results were obtained when the molar ratio of the carbonyl compound to reagent was at least 1:1. The failure to reduce esters with pyridine borane is probably a result of polymerization. The most

(7) A. B. Burg, Rec. Chem. Prog., 15, No. 4, 159 (1954).

vigorous reaction was observed with acid chlorides.

EXPERIMENTAL

Two procedures were employed in carrying out the reactions: (1) The reactants were dissolved in the chosen solvent and heated under simple reflux, and (2) the reagent was added dropwise to a refluxing solution of the carbonyl compound and solvent in an atmosphere of pure nitrogen. The reaction mixtures were hydrolyzed with dilute sodium hydroxide or dilute hydrochloric acid. The organic phase of the mixtures hydrolyzed with base was subsequently washed with dilute acid and then with water to remove the liberated pyridine, those hydrolyzed with acid were allowed to stand until the boric acid crystallized. The boric acid was removed by filtration, the solution washed with 10% sodium carbonate followed by water. After drying the organic phase with anhydrous sodium sulfate or potassium carbonate, the solvent was distilled. The resulting products were tested qualitatively for carbonyl compounds with 2,4-dinitrophenylhydrazine and for carbinols with ceric ammonium nitrate reagent. All liquid products except benzyl alcohol were positively identified through suitable solid derivatives. The solid products were identified by melting point and mixed melting point with authentic samples.

The results are shown in the following table.

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