and the oxidation procedure used for the preparation of 4,5-benzindole (V) was followed. The product (IV) was recovered from the steam distillate as white crystals; 0.45 g. (27%), m.p. 170–171°. By recrystallization from dilute ethanol an analytically pure sample (m.p. 172°) was prepared which gave a very strong positive test with Ehrlich's reagent. Its infrared spectrum in the 2.9 μ and 6.1 μ regions was similar to that of V.

Anal. Calcd. for $C_{12}H_9N$: C, 86.19; H, 5.43; N, 8.38. Found: C, 86.08; H, 5.40; N, 8.30.

Acknowledgment. This work was supported by a Frederick Gardner Cottrell Grant from the Research Corp.

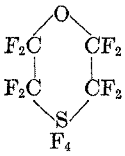
DEPARTMENT OF CHEMISTRY
COE COLLEGE
CEDAR RAPIDS, IOWA

Pyrolysis of Perfluorothioxane Tetrafluoride[1]

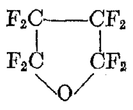
R. D. DRESDNER AND J. A. YOUNG

Received October 14, 1958

Fluorocarbon derivatives containing a SF_4 or SF_5 group have shown a marked tendency to pyrolyze[2,3] at much lower temperatures than fluorocarbon ethers or amines. The cyclic perfluorothioxane tetrafluoride (PTT), I, behaves similarly. Under a variety of pyrolysis conditions, the ether linkage is retained and SF_4 is eliminated. When PTT is pyrolyzed alone the recovered ether is perfluorotetramethylene oxide, II, when PTT is pyrolyzed in the presence of $CF_3N{=}CF_2$, perfluoro-2-azapropene, under some conditions II is a product while under other conditions perfluoroethyl ether $(C_2F_5)_2O$ results, plus other products.



I



II

EXPERIMENTAL

The PTT was prepared electrochemically in HF from thioxane.[4] It was purified by separation in large scale vapor phase chromatographic equipment.[5] Its properties were: b.p. 80.5°, m.p. 17.1–17.3°, n_D^{25} 1.3041. It had a purity of better than 99.5% by wt. as established by chromatographic analysis.

$CF_3N{=}CF_2$ was prepared from $(CF_3)_2NCOF$ by pyrolysis.[6]

Pyrolysis of PTT in a steel vessel. Forty g. (0.123 mole) of PTT was heated slowly in a 500 cc. stainless steel reaction vessel. At 325° and 8.8 atm. a sharp increase in pressure was noted. The pressure rose rapidly until it reached 18.7 atm. at 330° and then dropped over a 10-hr. period to 12 atm. When the vessel was evacuated, 28 g. of a clean liquid boiling below room temperature was recovered. The 12 g. of material not recovered were found in the vessel as elemental sulfur, 3.5 g., and FeF_3, 15.5 g. Apparently the SF_4 formed attacked the vessel and accounts for the solids and the associated drop in pressure under the conditions outlined. Twenty-five g. of the liquid boiled between 1.5 and 2.0°, had a mol. wt. of 216 and an infrared spectrum equivalent to that for $O(C_2F_4)_2$. The yield of the ether was not less than 90%.

Reaction of PTT with $CF_3N{=}CF_2$. Twenty-nine and a half grams. (0.22 mole) $CF_3N{=}CF_2$ and 20 g. (0.062 mole) PTT were heated in the 500 cc. (Hoke) reaction vessel to 336° at 22.6 atm. The isolated products amounted to 7.5 g. SF_4, 20.5 g. $CF_3N{=}CF_2$, mol. wt. 130–133, and 11.0 g. of material boiling at 1.5 to 4.5°. The last cut was washed with 20% NaOH, dried, and had a mol. wt. of 245–247. The infrared spectrum showed that it was preponderantly perfluoroethyl ether, $C_2F_5OC_2F_5$ (mol. wt. 254). The contaminant appeared to be the cyclic ether $O(CF_2)_4$. There was also 8 g. of material which boiled up to 150° without any temperature plateau. Part of it was reactive toward base, forming a white resinous solid.

A second similar trial was made with 25 g. $CF_3N{=}CF_2$ and 19 g. PTT at the lower temperature range of 260–277° and 17 atm. There was no serious pressure change over a 36-hr. heating period. Again, over the protracted heating period, much of the SF_4 produced attacked the vessel. The recovered products were 2.5 g. SF_4, 20.5 g. $CF_3N{=}CF_2$, 4.0 g. $C_2F_5OC_2F_5$ (mol. wt. 250) and 14 g. boiling up to 150°. The latter 14 g. was fractionated in a small column. A 2-g. fraction was isolated at 36–38° which had the correct properties for $(CF_3N{=}CF_2)_2$ [Reported b.p. 39°, mol. wt. 266, n_D^{25} 1.2596][7] mol. wt. 262–263 n_{25}^{D} 1.2606. The column did not reflux again until the head temperature reached 80°. There were 3 fractions (1) 80–123°, 2 g.; (2) 123–150°, 5 g.; (3) above 150°, 5 g. The latter two fractions were analyzed by gas chromatography and each showed 9 and 5 components respectively. These materials were not affected by base.

Flow pyrolysis of pure PTT. Some 40 g. of PPT (0.13 mole) was pyrolyzed in a vertical nickel reactor filled with NaF pellets without a carrier gas. It was flash-vaporized on a hot surface as it entered the reactor at the rate of 10 g./hr. Some 12 g. SF_4 and 22 g. of the cyclic ether were isolated from the reaction products. Only 4.5 g. of starting material were recovered. The yield of products was accordingly about 90%. The reaction temperature was 475°.

Flow reaction with PTT and $CF_3N{=}CF_2$. In this trial $CF_3N{=}CF_2$ was bubbled through PTT at 45°C. The $CF_3N{=}CF_2$ was present in the reaction mixture molewise in six fold excess. The mixture was fed into a nickel reactor packed with NaF pellets at the rate of 10 g./hr. at 430°. However, except for the decomposition of PTT to form SF_4 and II, no other reactions were in evidence.

Reaction of $CF_3N{=}CF_2$ and PTT at over 75 Atm. This final reaction was to determine the effect of high pressure. Sixty g. of each reactant were charged in a stainless steel pressure reactor (Aminco) and heated for 40 hr. at between 290 and 320° at from 75.6 to 79.2 atm. In the main the temperature did not exceed 300° until near the end of the trial. The products found were SF_4 and II in the usually good

---

(1) This work was supported by the Chemistry Branch, Office of Naval Research; all or any part of this paper may be reproduced for purposes of the United States Government.

(2) R. D. Dresdner, *J. Am. Chem. Soc.*, **77**, 6633 (1955).

(3) R. D. Dresdner, *J. Am. Chem. Soc.*, **79**, 69 (1957).

(4) R. D. Dresdner and J. A. Young, *J. Am. Chem. Soc.*, **81**, 574 (1959).

(5) T. M. Reed, J. F. Walter, R. R. Cecil, and R. D. Dresdner, *Ind. & Eng. Chem.*, **51**, 271 (1959).

(6) J. A. Young, T. C. Simmons, and F. W. Hoffman, *J. Am. Chem. Soc.*, **78**, 5637 (1956).

(7) J. A. Young, W. S. Durrell, and R. D. Dresdner, 134th Meeting A.C.S. Chicago, Ill., September 1958.

yields but in incomplete conversions. Fourteen g. of PTT were recovered despite the long heating period. The only other product was a 4-g. fraction of the $CF_3N{=}CF_2$ dimer. There was no material boiling above 80.5°.

Acknowledgment. Support of this work by the Chemistry Branch, Office of Naval Research is gratefully acknowledged.

DEPARTMENTS OF CHEMICAL ENGINEERING AND
CHEMISTRY
UNIVERSITY OF FLORIDA
GAINESVILLE, FLA.

A New Procedure for the Dehydrogenation of Flavanones with *N*-Bromosuccinimide[1]

J. H. LOOKER AND MYRON J. HOLM[2,3]

Received October 17, 1958

The application of *N*-bromosuccinimide (NBS) to dehydrogenation of flavanone derivatives has been reported by Lorette, Gage, and Wender,[4] who converted flavanone glycosides to flavone glycosides, and subsequently by a number of workers[5] to dehydrogenation of other flavanone derivatives. In each case, the essential steps were bromination with *N*-bromosuccinimide and dehydrohalogenation of the bromination product with an organic or inorganic base. It is noteworthy that two groups[5b,6] described the bromination mixture as assuming a reddish-brown color, which later disappeared. In the present note, we report that the usual NBS dehydrogenation procedure can be modified by removing by-product bromine, with marked improvement in the yield of flavone.

In applying the NBS reaction to hesperetin triacetate (4′-methoxy-3′,5,7-triacetoxyflavanone) we observed rapid development of a reddish-brown product. Since this substance was volatile with the carbon tetrachloride vapors and blackened moist starch-iodide paper, it was considered to be bromine. Concomitant formation of hydrogen bromide could not be detected. Later, the bromine-red color increased in intensity, but after the solid NBS had disappeared, diminished rapidly and finally faded completely. Hydrogen bromide was evolved during this late reaction stage. In another experiment, the solvent, carrying with it bromine, was distilled from the reaction vessel and collected. Titration of the distillate with standard sodium bisulfite solution showed that it contained most of the bromine originally present in the NBS. The residue afforded a good yield of diosmetin triacetate (sequel).

These observations are interpreted as indicating that the NBS first brominated the flavanone, possibly in the 2-position.[7] Then the bromoflavanone yielded the flavone by elimination of hydrogen bromide, which attacked unreacted NBS to produce bromine and succinimide.[8] A possible final step would be bromination of the flavone by free bromine. This sequence, which is somewhat similar to that proposed by Stuckwisch and coworkers[9] in their study of the oxidation of alcohols by NBS, is shown in Chart 1.

(1) Flavanone + NBS $\longrightarrow$
2- or 3-Bromoflavanone + Succinimide

(2) Bromoflavanone $\longrightarrow$ Flavone + HBr

(3) HBr + NBS $\longrightarrow$ Br_2 + Succinimide

(4) Flavone + Br_2 $\longrightarrow$ Brominated flavone + HBr

CHART I

A practical result of these observations has been development of a new procedure for the dehydrogenation of flavanones. From Chart 1, it is apparent that step (4) would be undesirable, and the key step in our procedure is removal of bromine by distillation. This method affords an alternative to the recently described neutralization of hydrogen bromide in NBS reaction mixtures[9] which also prevents deleterious side reactions due to bromine. The flavanone in carbon tetrachloride solution was

---

(1) This investigation was supported by a research grant (E-1703) from the National Institute of Allergic and Infectious Diseases, Public Health Service.

(2) DuPont Postgraduate Teaching Assistant, 1956–1957; Standard Oil of Indiana Foundation Fellow, 1957–1958.

(3) Abstracted from a portion of the Ph.D. thesis of Myron J. Holm, University of Nebraska, 1958.

(4) N. B. Lorette, T. B. Gage, and S. H. Wender, *J. Org. Chem.*, **16**, 930 (1951).

(5) (a) R. C. Chen and C. H. Yang, *J. Taiwan Pharm. Assoc.*, **3**, 39 (1951); *Chem. Abstr.*, **49**, 10277 (1955); (b) N. R. Bannerjee and T. R. Seshadri, *Proc. Indian Acad. Sci.*, **36A**, 134 (1952); (c) S. Hishida, S. Sasaki, M. Suzuki, and M. Takatori, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **74**, 697 (1953); *Chem. Abstr.*, **48**, 12094 (1954); (d) K. Nakagawa and H. Tsukashima, *J. Chem. Soc. Japan*, **75**, 485 (1954); Chem. Abstr. **51**, 11339 (1957); (e) R. Bognar and M. Rakosi, *Chem. & Ind. (London)*, **1955**, 773; (f) H. R. Arthur, W. H. Hui, and C. N. Ma, *J. Chem. Soc.*, **1956**, 632.

(6) G. W. K. Cavill, F. M. Dean, A. McGookin, B. M. Marshall, and A. Robertson, *J. Chem. Soc.*, **1954**, 4573.

(7) This possibility is based partly on the observation of Stuckwisch and co-workers [ref. (9)] that bromination of the position *alpha* to a carbonyl group in certain ketones is effected by by-product bromine rather than by the primary reactant, NBS. In addition, we have noted (unpublished observations) that the 3-bromohesperetin triacetate of G. Zemplen and R. Bognar [*Ber.*, **76B**, 454 (1943)] does not undergo elimination of hydrogen bromide under the conditions of the NBS reaction.

(8) An observation that a very unstable bromo compound can undergo dehydrohalogenation before bromination is complete, liberate free bromine by reaction of evolved hydrogen bromide with NBS, and cause side reactions due to bromine has been recorded by P. Wieland and K. Miescher, *Helv. Chim. Acta*, **30**, 1876 (1947). Also see R. A. Barnes *J. Am. Chem. Soc.*, **70**, 145 (1948), who attributed an orange-red color in NBS reaction mixtures to the equilibrium, HBr + NBS $\rightarrow$ succinimide + Br_2, and stated that it is diagnostic for HBr in the mixture.

(9) C. G. Stuckwisch, G. G. Hammer, and N. F. Blau, *J. Org. Chem.*, **22**, 1678 (1957).