200°. All except 8.5% of the tritium wax taken up by the lithium borohydride; the remaining gaseous tritium was converted to tritiated water.[5] Dry tetrahydrofuran (10 ml.) and 1.1890 g. of dry ethyl acetate were distilled into the flask containing tritium-enriched borohydride. The contents of the flask were warmed slowly and kept at reflux temperature for 8 hr. The solvent and a small amount of excess ester was removed by distillation. Twenty-five ml. of hydrobromic acid (Baker's Analyzed Reagent) was added slowly to the flask through a dropping funnel while the reflux condenser was cooled with water. The flask was heated to 90° for 2.5 hr. while a stream of nitrogen was passed through it and then through a trap immersed in liquid nitrogen. When the reaction was complete, the product in the trap was purified on the vacuum line, and only material boiling above −85° and lower than −58° at 1 micron pressure was retained. The vapor pressure of the product at 27° was 494 mm. compared to 475 mm. at 25.5° for a known sample of ethyl bromide. The radioactive ethyl bromide weighed 1.783 g.

Preparation of 3,4-dianisyl-2-t-3-hexene. A Grignard solution was prepared from the above ethyl bromide, 1.102 g. of non-radioactive ethyl bromide, 0.6398 g. of magnesium, and 20 ml. of diethyl ether. A solution of 7.51 g. of α-ethyldesoxyanisoin[6] in 10 ml. of ether was added and the mixture was refluxed. After 2 hr. the reaction flask had an oily layer at the bottom, indicating excess ketone. Another Grignard solution prepared from 5.77 g. of ethyl bromide and 1.50 g. of magnesium was added to the flask to insure complete reaction of the ketone. The mixture was hydrolyzed in acidified water and ice and worked up in the usual way.[7] A white solid weighing 6.07 g. and melting at 75–95° was obtained. Two forms of 3,4-dianisyl-3-hexanol have been reported,[8] one melting at 114–117° and one at 83–85.5°; the solid product was assumed to be a mixture of these two forms.

This mixture was dehydrated by the method of Wilds and Biggerstaff[8] with *p*-toluenesulfonic acid at 125–130° with a weight yield of only 35%. A total of 1.58 g. of active 3,4-dianisyl-3-hexene was obtained melting at 122.5–123.5° (literature,[6] 123–124°) with an activity of 5.02 mc./g.

DEPARTMENT OF CHEMISTRY
OKLAHOMA STATE UNIVERSITY
STILLWATER, OKLA.

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A New Indole Synthesis

F. C. PENNINGTON, M. JELLINEK, AND R. D. THURN

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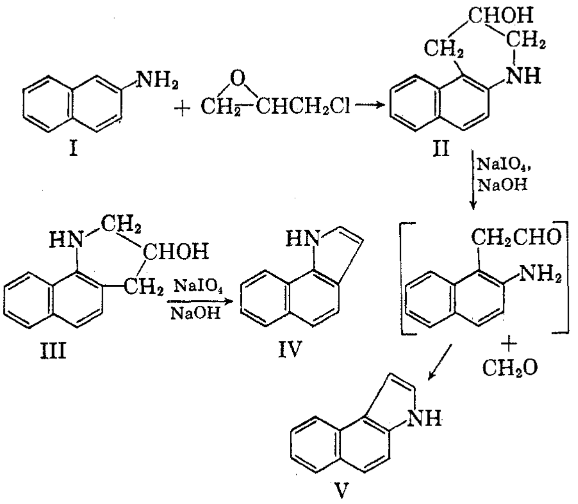
It is known that when hydroxyproline is oxidized with periodate, formaldehyde is split out and presumably an amino aldehyde is formed.[1] It would be expected that properly substituted β-hydroxypiperidines would likewise be oxidized, and the amino aldehydes thus formed might be cyclized to give indoles. Lange and others[2] have reported the synthesis of suitable β-hydroxypiperidines, II and III, by the reaction of epichlorohydrin with β-naphthylamine and α-naphthylamine, respectively. The oxidation of II and III was investigated, therefore, and has led to the synthesis of 6,7-benzindole (IV) in 27% yield and the picrate of 4,5-benzindole (V) in 30% yield.



EXPERIMENTAL

Preparation of 4,5-benzindole (V) *by periodate oxidation of* II. II (2.00 g.) was dissolved in 50 ml. of ethanol and sodium metaperiodate (2.14 g.) was dissolved in 50 ml. of water. These solutions were added dropwise over a 3-hr. period to a 100-ml. solution of 8% sodium hydroxide through which steam was passing rapidly. The steam distillate was collected until the distillate no longer gave a red color with an acidic alcoholic solution of dimethylaminobenzaldehyde (Ehrlich's reagent). This required about 7 hr. The distillate was then extracted with benzene, the benzene extract dried over sodium sulfate, and the benzene removed *in vacuo*. The residual oil was dissolved in ethanol and treated with an ethanolic picric acid solution. Red needles of the picrate of V were recovered and dried; 1.20 g. (30%), dec. 205° with previous charring.

Anal. Calcd. for $C_{18}H_{12}N_4O_7$: C, 54.55; H, 3.05; N, 14.14. Found: C, 54.28; H, 3.20; N, 14.26.

An alkaline solution of the picrate was extracted with ether, and the ether extract was dried over potassium carbonate. The ether was removed, and the residual oil distilled, b.p. 145–150°/5 mm. The oil was purified further by dissolving it in benzene and chromatographing it on alumina. A sample boiling at 148°/5 mm. was analyzed.

Anal. Calcd. for $C_{12}H_9N$: C, 86.19; H, 5.43; N, 8.38. Found: C, 85.93; H, 5.45; N, 8.28.

An infrared spectrum of the oil (V) in chloroform showed a strong sharp band close to 2.9 μ but only weak absorption around 6.1 μ.

Preparation of 6,7-benzindole (IV) *by the oxidation of* III. Compound III (2.00 g.) was dissolved in 100 ml. of ethanol,

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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.

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COE COLLEGE
CEDAR RAPIDS, IOWA

Pyrolysis of Perfluorothioxane Tetrafluoride[1]

R. D. DRESDNER AND J. A. YOUNG

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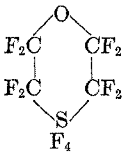
Fluorocarbon derivatives containing a SF_4 or SF_5 group have shown a marked tendency to pyrolyze[2,3] at much lower temperatures than fluorocarbon ethers or amines. The cyclic perfluorothioxane tetrafluoride (PTT), I, behaves similarly. Under a variety of pyrolysis conditions, the ether linkage is retained 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.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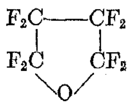
II

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

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(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.

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