The formation of the photoadducts, IIa and IIb, which involves a polar intermediate, does not appear to have any parallel in the photoreaction of α,β-unsaturated ketones in alcoholic solvents.[14] Although the nature of this addition reaction has not been determined, we wish to mention three possible explanations. First, the addition can simply arise from alcohol opening up the phenonium ion VIIa which is formed from the n–π^* excited state of I.[5a] Second, it is possible that the π–π^* excited state, which is classically pictured as $^+C—C{=}C—O^-$,[15] is involved in the reaction. Third, it is also reasonable to assume that an interaction between the π orbitals of the benzene and enone groups of I leads to a polar intermediate whose β-carbon atom of the carbonyl group is electron deficient. Inspection of a scale model demonstrates that the distance (*ca.* 4 A) between the centers of both chromophores in I is enough close to interact each other. Such an interaction may be suggested by an unusual bathochromic shift[16,16a] of the ultraviolet maximum (302 mμ (log ϵ 3.39)) of I compared to those of IIa (284 mμ (log ϵ 3.58)) and of the dihydro derivative of I[17] (286 mμ (log ϵ 3.58)).

The scope, limitations, and detailed mechanism are being studied in our laboratory.

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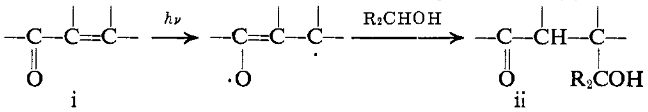
(14) It has been reported that irradiation of some α,β-unsaturated ketones (i) in a primary or secondary alcohol give adducts (ii) which are formed by a radical process: M. Pfau, R. Dulou, and M. Vilkas, *Compt. Rend.*, **254**, 1817 (1962); I. A. Williams and P. Blandon, *Tetrahedron Letters*, 257 (1964).



(15) S. F. Mason, *Quart. Rev.* (London), **15**, 287 (1961).

(16) This has analogy in the spectrum of flavothebaone (A. I. Scott, "Interpretation of the Ultraviolet Spectra of Natural Products," Pergamon Press, New York, N. Y., 1964, p 347). It should be noted that only normal benzenoid absorption and the usual unsaturated ketone absorption with a typical n–π^* band have been observed in the spectrum of 4a-methyl-4,4a,9,10-tetrahydro-2(3H)-phenanthrone, which on irradiation in methanol gives exclusively a photoisomer *via* path B.[5c] We are indebted to Dr. H. E. Zimmerman for his information of the spectra data.[16a]

(16a) Note Added in Proof. It should be also noted that in dilute acetic acid the above phenanthrone gives Michael-type addition products in low yields.[3b]

(17) D. H. R. Barton, A. M. Deflorin, and O. E. Edwards, *J. Chem. Soc.*, 530 (1956).

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Trifluoramine Oxide

Sir:

We wish to report the synthesis and characterization of the unusual new compound trifluoramine oxide, F_3NO, first member of the hitherto unknown perfluorinated amine oxides.[1] The new compound, bp $-85°$, mp $-160°$, was identified by chemical analysis (Calcd: F, 65.5; N, 16.1. Found: F, 66.2; N, 16.0), molecular weight (Calcd: 87.0. Found, 86.8), and mass spectroscopy (principal fragments F_2NO^+, FNO^+, NO^+, NF^+). The F^{19} nmr spectrum (56.4 Mc/sec) of liquid F_3NO at $-90°$ consists of a sharply defined 1:1:1 triplet at δ_{CCl_3F} -363 ± 2 ppm with $J_{NF} = 136$ cps, indicating that the fluorine atoms are equivalent and bonded to nitrogen in the highly symmetrical environment expected of an amine oxide structure.

The nearly tetrahedral C_{3v} symmetry of F_3NO is further manifested in the infrared spectrum of the molecule, with fundamental bands (cm^{-1}) and assignments as follows: 1687 (vs), N–O stretch; 743 (s), sym N–F stretch; 558 (vw), sym NF_3 deformation; 887 (vvs), unsym N–F stretch; 528 (s), F–N–O deformation; 398 (w), unsym NF_3 deformation. These represent the modes ν_1 through ν_6, respectively, the first three being type A (with PQR branching) and the last three of type E, as required by the C_{3v} symmetry. Other bands observed were at 3345 (m), 2435 (w), 1772 (s), 1622 (w), 1410 (m), 1055 (m), 929 (w), and 801 (w) cm^{-1}. A complete normal coordinate analysis of the vibrational spectrum of F_3NO has been carried out and will be published elsewhere.[2]

Trifluoramine oxide can be prepared in 10–15% yields by the action of an electric discharge (5000 v, 30 ma) on equimolar NF_3–O_2 mixtures at $-196°$. The apparatus and techniques used were similar to those employed by others for the electric discharge syntheses of O_2F_2 and O_3F_2 from oxygen and fluorine.[3] The crude product was fractionated through traps at -140, -160, and $-196°$, the F_3NO collecting in the $-160°$ trap.

Trifluoramine oxide is a strong oxidizing agent toward many organic and inorganic materials but is resistant to hydrolysis even by strong aqueous bases. The latter property is useful in purification, since common impurities (SiF_4, NO_2, NOF, NO_2F) are easily removed by scrubbing with strong aqueous KOH solution without significant loss of F_3NO. Carefully purified F_3NO is stable in glass and most metals at 25° and can be recovered intact after heating to 300° in nickel or Monel vessels. The compound adds to some fluorinated olefins to form the corresponding $RONF_2$ derivatives.

Trifluoramine oxide forms stable 1:1 complexes with AsF_5 and SbF_5. These complexes are probably ionic (*e.g.*, $F_2NO^+MF_6^-$) since the F^{19} nmr spectrum of each in HF solution shows a 4:5:4 triplet N–F resonance at δ_{CCl_3F} -331 ± 3 ppm ($J_{NF} = 250$ cps) along with the high-field resonance of the corresponding MF_6^- anions[4] (AsF_6^-, 60 ppm; SbF_6^-, $+135$ ppm) in HF solution. The area of the low-field N–F resonance is one-third that of the high-field MF_6^- resonances. Infrared spectra of thin films of the solid complexes show strong bands at 1857, 1162, and 905 cm^{-1} (N=O, sym N–F, asym N–F stretches, respectively), along with the appropriate MF_6^- bands.

Photolysis of F_3NO at $-196°$ produces the relatively stable $F_2NO\cdot$ radical, identified by its nine-line esr spectrum with $a_N = 94.3$ gauss, $a_F = 142.2$ gauss, and $g = 2.009$. A more complete account of the preparation and chemistry of F_3NO will be presented in a forthcoming series of publications.

Acknowledgment. This research was supported by the Advanced Research Projects Agency, Propellant

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(1) As this manuscript was being prepared for publication, we learned of the independent discovery of F_3NO by others: N. Bartlett and S. P. Beaton, *Chem. Commun.*, 167 (1966); N. Bartlett, S. P. Beaton, and N. K. Jha, *ibid.*, 168 (1966). These workers found F_3NO as a trace product in reactions of OsF_6 and PtF_6 with nitric oxide, but gave no details of its properties. We are grateful to Professor Bartlett for preprints of his work.

(2) J. R. Holmes, J. S. MacKenzie, and W. B. Fox, to be published.

(3) A. D. Kirshenbaum and A. V. Grosse, *J. Am. Chem. Soc.*, **81**, 1277 (1959).

(4) B. B. Stewart and C. A. Wamser, unpublished results.

Chemistry Office, and was monitored by Army Research Missile Command, Redstone Arsenal, Huntsville, Alabama, under Contract No. DA-30-069-ORD-2638.

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Chemical Synthesis of a Stereoregular Linear Polysaccharide

Sir:

We wish to report the chemical synthesis of poly-α-(1→6)-anhydro-D-glucopyranose by an essentially stereospecific method. Highly purified 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-glucopyranose[1] was dissolved in methylene chloride and treated at −78° with phosphorus pentafluoride freshly generated from an aryldiazonium hexafluorophosphate. All final purifications, transfers, degassings, and the polymerization itself were carried out on the rack using standard high-vacuum techniques. Ranges of 10–20 mole % catalyst to monomer and 20–30% concentrations of monomer resulted in the formation of polymer of number-average molecular weights from 42,000 to 76,600, with molecular rotations from +472 to +489° and intrinsic viscosities from 0.25 to 0.38. Polymerizations of related derivatives were shown to produce broad and variable molecular weight distributions, and apparently the same result was obtained with the tribenzyl derivative, for the intrinsic viscosities of a few reaction products were not directly related to their respective number-average molecular weights.

Debenzylation was accomplished by the slow addition of polymer in pure dimethoxyethane to a solution of a sevenfold excess of sodium in liquid ammonia. After 1 hr of stirring, an equimolar amount of ammonium chloride was added and solvents were removed under a stream of nitrogen. The solids were slurried with methylene chloride, separated, dissolved in water, dialyzed against distilled water, concentrated, clarified by centrifugation, and freeze dried. This debenzylation and work-up gave 80–85% conversion to a water-soluble ash-free dextran-like polymer, which showed no benzylic absorption at 250–270 mμ. Polymers dried *in vacuo* at room temperature retained tenaciously one molecule of water/two glucose units (*Anal.* Calcd for $(C_6H_{10}O_5)_2H_2O$: C, 42.10; H, 6.48. Found: C, 41.92; H, 6.49) and even at 100° failed to lose additional weight.

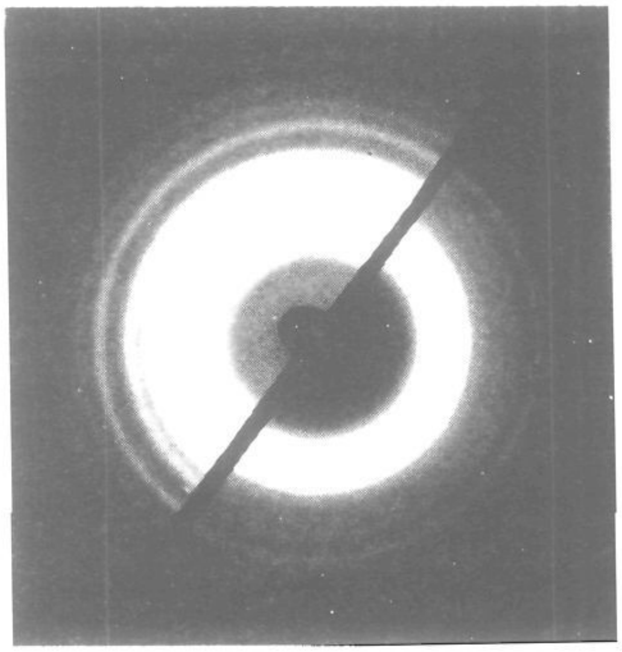

Figure 1. X-Ray powder diagram of synthetic and natural polysaccharides. Upper left, synthetic linear dextran hemihydrate; lower right, natural slightly branched dextran.

These polysaccharides, like the natural dextrans,[2] dissolved best in cold water, ∼5°, to form slightly opalescent solutions, but during preparation of solutions at room temperature a small portion crystallized sufficiently to remain insoluble in water. Their intrinsic viscosity in water at 30° ranged from 0.180 to 0.191. From the viscosity–molecular weight relationship determined for natural dextrans which are believed to have only a few short branches[3] and a relatively narrow molecular weight distribution ($\overline{M}_w/\overline{M}_n = 1.58$)[4] this would correspond to $\overline{M}_v$ from 32,400 to 36,500 or $\overline{DP}_v = 200$ to 225.

The X-ray diagram of films of the synthetic polymer differed from that of a slightly branched natural dextran (Pharmacia Dextran 20 Lot No. To 536) of similar molecular weight, the pattern of the synthetic polymer showing higher crystallinity and different ring spacings (Figure 1).[5] The infrared spectrum resembled that of glucose closely except that the C-1 axial hydrogen deformation band at 891 ± 7 cm^{-1} characteristic of the β linkage[6] appeared to be absent. By solvent precipitation with ethanol, a lower molecular weight fraction (∼10%) was eliminated and the optical rotation of the product was raised from $[\alpha]^{25}\text{D}$ +196 to +200° (water) (corrected for water content of the polymer). The rotation of both Pharmacia and Northern Regional Research Laboratory B-512 natural dextrans is $[\alpha]^{25}\text{D}$ +199 (water).[2] It is surprising that the correspondence of the rotational values for the synthetic and natural polymers is so good since the small fraction of α-(1→3) linkages in the natural polymer are more dextrorotatory than the α-(1→6) (see ref 7).[2]

The expanded nmr spectrum of the synthetic deuterated dextran in D_2O contained an intense C-1 equatorial hydrogen resonance at δ 5.05[8] and there was no C-1 axial proton resonance at δ 4.5–4.6,[9,10] although it would have been observed if 1 or 2% of the linkages were of the β configuration. Integration of the spectrum gave the expected proton ratio of six for ring and primary equatorial anomeric hydrogens.

This appears to be the first reported stereospecific chemical synthesis of a linear polysaccharide. The high stereospecificity of the process is understandable

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[3] M. Wales, P. A. Marshall, and S. G. Weissberg, *J. Polymer Sci.*, **10**, 229 (1953).

[4] Determined by Pharmacia, Uppsala, Sweden, on similar Dextran 40 Lot No. To 4931. This dextran is the most linear variety obtainable from Pharmacia.

[5] Determined by G. Quigley, this laboratory.

[6] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, Inc., New York, N. Y., 1965, p 395.

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