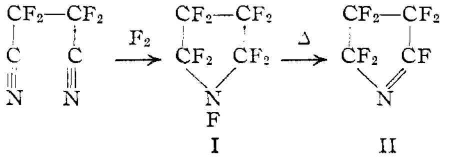

This transformation was accomplished by passing I on a stream of dry nitrogen through a stainless steel tube packed with steel gauze and maintained at 500°. After purification by preparative chromatography, II was a colorless liquid, b.p. 22° (extrapolated), and mol. wt. 198 ± 4 (calcd. 195). The infrared spectrum showed a sharp band at 5.81 μ which has been assigned to the $C{=}N$ stretching vibration. When II reacted with an excess of 10% NaOH solution in a sealed tube for 24 hours at room temperature, it was hydrolyzed to ammonia, sodium carbonate and sodium tetrafluorosuccinate. The latter was identified by comparing its infrared spectrum with that of an authentic sample prepared by the oxidation of 1,2-dichlorotetrafluorocyclobut-1-ene.[3] The free acid, obtained by the acidification and ether extraction of the hydrolysis product, gave an anilinium salt, m.p. 223–225°. A mixture melting point with a sample of the dianilinium salt of tetrafluorosuccinic acid[4] showed no depression.

Subsequent to the submission of this communication, II has been claimed by Ulrich,[5] who presented only an unconvincing elemental analysis in support of this assignment. His reported boiling point for II of 56 to 58° is unreasonable in view of the close relationship between structure and boiling point which has been observed for highly fluorinated organic compounds.

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[3] A. L. Henne and W. F. Zimmer, *J. Am. Chem. Soc.*, **73**, 1103 (1951).

[4] M. W. Buxton, *et al.*, *J. Chem. Soc.*, 3830 (1952).

[5] H. Ulrich, *et al.*, *J. Org. Chem.*, **27**, 2585 (1962).

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THE BECKMANN REARRANGEMENT OF KETOXIMES: A NEW METHOD

Sir:

The Beckmann rearrangement has widespread synthetic applications.[1] Experimental procedures[1] frequently involve the use of strongly acidic reagents or of elevated temperatures, causing isomerization of the oximes prior to rearrangement. We now wish to report a facile and rapid general method of Beckmann rearrangement of immediate utility for the synthesis of amides and lactams.

A solution of the ketoxime in acetone was treated at 0° with successive equimolar quantities of 8% aqueous sodium hydroxide solution and of benzene(or *p*-toluene)-sulfonyl chloride, and the mixture shaken at 0° for ten minutes. Removal of acetone *in vacuo* at 25° gave a quantitative yield of the benzene(or *p*-toluene)-sulfonate ester (which may be isolated in the usual manner). The crude ester was taken up in benzene and the benzene solution, concentrated *in vacuo* at 25° to a small volume, was poured onto a column of alumina (Brockmann activity I or II, alkaline or acid-washed; *ca.* 25 g. of alumina per g. of ester) covered with hexane. Unreacted sulfonyl chloride was removed by washing with hexane, and elution with benzene containing an increasing proportion of chloroform then gave the pure amide or lactam, usually in almost quantitative yield.

In this manner methyl 2-thienyl ketoxime, m.p. 112–113°, gave first the oxime benzenesulfonate, m.p. 85–86°, and then 2-acetamidothiophene, m.p. 161°, in 90% yield. The isomeric unstable methyl 2-thienyl ketoxime, m.p. 81–84°, afforded an oxime benzenesulfonate, m.p. 83–84° (preparation to be described) and thence 66% N-methylthiophene-2-carboxamide, m.p. 112–114°. *tert*-Butyl 2-thienyl ketoxime, m.p. 142–144°, yielded a benzenesulfonate ester, m.p. 67–68°, converted to 40% pure N-*tert*-butylthiophene-2-carboxamide, m.p. 147–148°. Phenyl 2-thienyl ketoxime, m.p. 114–116°, gave 90% thiophene-2-carboxanilide, m.p. 143–144.5°; and benzophenone oxime afforded 90% benzanilide. Finally 5-α-cholestane-3-one oxime, m.p. 199–201°, gave (*via* the *p*-toluenesulfonate ester, prepared in pyridine instead of acetone) 85% of pure 3-aza-A-homo-5-α-cholestane-4-one,[2,3] m.p. 271–273°.

Satisfactory analytical and spectroscopic data were obtained for all new compounds reported herein, and identity of all products was confirmed by mixed melting points with authentic samples.

The only previous report of the Beckmann rearrangement of a ketoxime ester by chromatography on alumina appears to be the production of benzanilide on attempted purification of benzophenone oxime diphenylphosphate.[4]

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[1] L. G. Donaruma and W. Z. Heldt, *Organic Reactions*, **11**, 1 (1960).

[2] C. W. Shoppee and J. C. P. Sly, *J. Chem. Soc.*, 3458 (1958).

[3] N. J. Doorenbos and H. Singh, *J. Pharm. Sci.*, **51**, 418 (1961).

[4] J. H. Turnbull, *Chem. and Ind.*, 350 (1956).

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1,3-DITHIOLIUM SALTS; A NEW PSEUDOAROMATIC CATION

Sir:

The 1,3-dithiolium system heretofore has been known only in the form of benzo[1,2] and aryl[3] derivatives, although LCAO-MO. calculations[4] suggested that the existence of the parent cation was "probable." We have obtained 1,3-dithiolium hydrogen sulfate (IIa) in 80% yield by peracetic acid oxidation of 1,3-dithiole-2-thione (I) in acetone solution; this reaction earlier proved valuable in the synthesis of 1,2-dithiolium salts.[5]

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[1] W. R. H. Hurtley and S. Smiles, *J. Chem. Soc.*, 1821 (1926); 534 (1927).

[2] L. Soder and R. Wizinger, *Helv. Chim. Acta*, **42**, 1733, 1779 (1959).

[3] D. Leaver and W. A. H. Robertson, *Proc. Chem. Soc.*, 252 (1960).

[4] J. Koutecký, J. Paldus and R. Zahradník, *Coll. Czechoslov. Chem. Commun.*, **25**, 617 (1960), *cf.* R. Zahradník and J. Koutecký, *Tetrahedron Letters*, 632 (1961).

[5] E. Klingsberg, *J. Am. Chem. Soc.*, **83**, 2934 (1961).