

PERFLUOROTETRAMETHYLFURAN

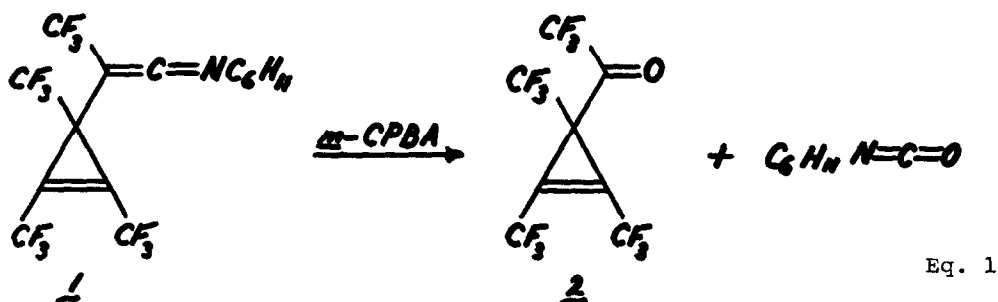
Clinton J. Boriack<sup>1</sup>, Evan D. Laganis, and David M. Lemal<sup>\*</sup>

Department of Chemistry, Dartmouth College  
Hanover, New Hampshire, U.S.A. 03755

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Kobayashi's novel synthesis of the previously unreported title compound (see accompanying paper) prompts us to record our own somewhat unusual synthesis of this heterocycle, discovered during a search for routes to the  $(\text{CCF}_3)_4$  valence isomers.

Several years ago, Oakes<sup>2</sup> showed that perfluoro-2-butyne reacts with cyclohexyl isocyanide to yield ketenimine 1 (63% in our hands). When treated with *m*-chloroperbenzoic acid (2.5 equivalents) in 1,2,4-trichlorobenzene, 1 reacts exothermically to give the cyclopropenyl ketone 2 and cyclohexyl isocyanate (Eq. 1). This reaction is performed in a stirred reaction vessel which is evacuated



through a liquid nitrogen-cooled U-trap to ~0.1 Torr; a single bulb-to-bulb distillation of the trap contents affords pure ketone in 85% yield. B.p. 73-74°; ir(neat) 1927( $\nu_{\text{C}=\text{C}}$ ), 1770( $\nu_{\text{C}=\text{O}}$ ), 1300-1140( $\nu_{\text{C}-\text{F}}$ ), 994, 922, 854, 698  $\text{cm}^{-1}$ ; uv (cyclohexane)  $\lambda_{\text{max}}$  289(39), 302(46), 313(45),  $\lambda_{\text{sh}}$  271, 279, 323, 338 nm; ms m/e

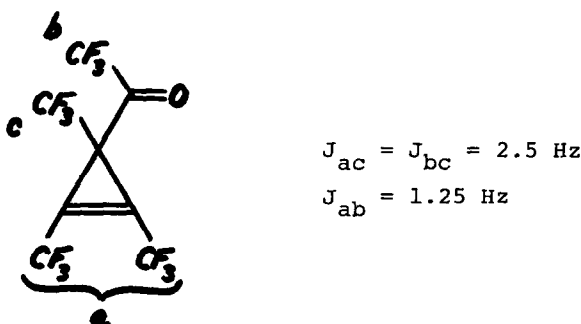
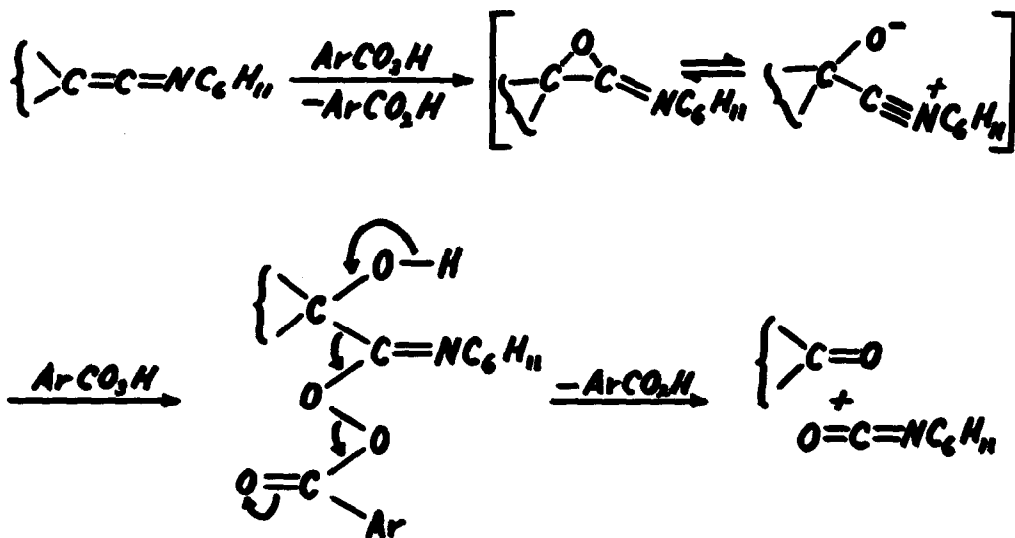


Fig. 1. Spin-spin coupling in 2.

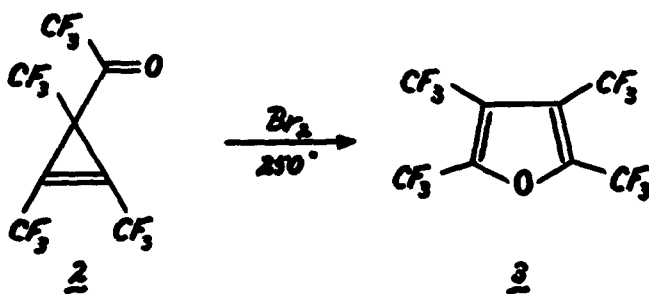
340 (parent), 243 (base, perfluorotrimethylcyclopropenium ion);  $^{19}\text{F}$  nmr (Fig. 1)<sup>3</sup> 60.73 (a, symmetrical decet), 67.23 (b, symmetrical tridecet), 74.79ppm (approximately binomial decet), relative areas 2:1:1.

A possible pathway for this efficient oxidation is shown in Scheme 1.<sup>4</sup>

Scheme 1.



Despite the strain in its skeleton, ketone **2** is very stable to heat,<sup>5</sup> polymerizing rather slowly at 350°. The compound stoutly resists thermal addition of bromine; under forcing conditions it yields, not an adduct, but an isomer: perfluorotetramethylfuran (**3**, Eq. 2).<sup>6</sup> In a typical experiment, the ketone is heated with 0.6 equivalents of bromine at 250° for 13 hours in a Pyrex ampoule.

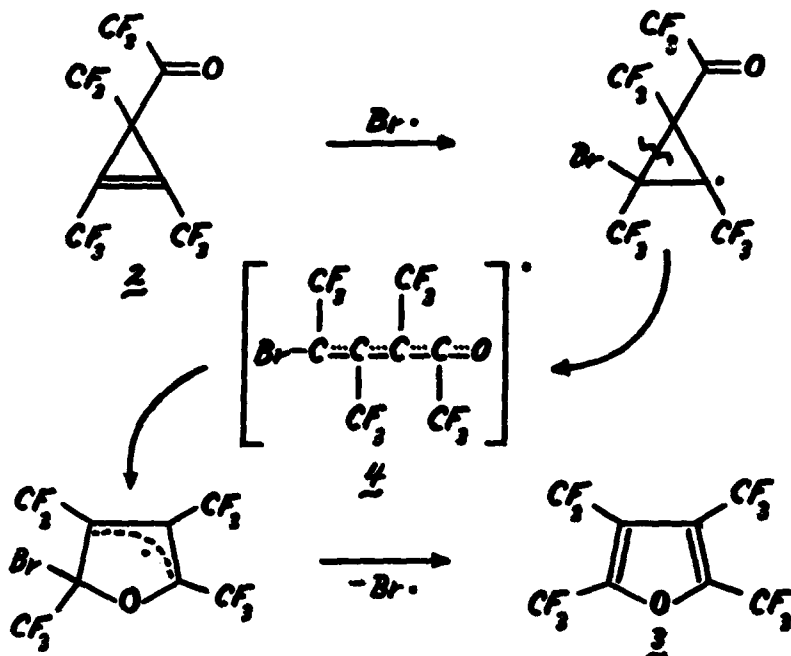


Eq. 2

After decolorization of the product with zinc dust, a single transfer in vacuo gives pure 3 in 95% yield. B.p. 104-105°; ir (neat) 1643, 1446, 1285, 1270-1140, 980, 758, 745, 711  $\text{cm}^{-1}$ ; uv (vapor)  $\lambda_{\text{max}}$  202 nm; ms m/e 340 (parent), 321 (base, -F);  $^{19}\text{F}$  nmr<sup>4</sup> 57.70, 62.62ppm (symmetrical multiplets of equal area).

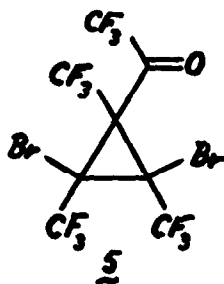
The bromine-catalyzed isomerization<sup>7</sup> of 2 may well proceed via bromine atom attack, as proposed in Scheme 2. Only two of the eight possible stereoisomers of 4 can close to the five-membered ring, but the necessary configurations may be attained by reversible formation of 4 from 2, by reversible formation of dibromides

Scheme 2.



from 4, and/or by rotation about the partial double bonds of 4.

Irradiation with a sunlamp of a carbon tetrachloride solution containing ketone 2 and bromine yields a stereoisomeric mixture of dibromides (5), whose chemistry will be discussed in a later paper. Elimination of bromine from 5 occurs at temperatures above 200°, again giving perfluorotetramethylfuran.



Attempts to photoisomerize the furan to its Dewar form, in analogy to perfluorotetramethylthiophene's photochemistry,<sup>8</sup> have met with failure.

Replacement by perfluoroalkyl groups of fluorines attached to strained and/or unsaturated carbon skeletons normally results in very different properties and behavior. This generalization is strikingly borne out by perfluorotetramethylfuran and perfluorofuran. The great thermal stability and resistance to bromine of the former stands in sharp contrast to the spontaneous polymerization and facile bromine addition characteristic of the latter.<sup>9</sup>

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#### References and Notes

- 1) Present address: Dow Chemical Company, Freeport, Texas, USA 77541.
- 2) T.R. Oakes, H.G. David, and F.J. Nagel, J. Amer. Chem. Soc., 91, 4761 (1969).
- 3) Nmr spectra were measured in  $\text{CFCl}_3$ , and chemical shifts are reported in ppm upfield from the solvent signal.
- 4) For a closely-related oxidative fragmentation of enol ethers brought about by  $m$ -CPBA, see I. Borowitz, G. Gonis, R. Kelsey, R. Rapp, and G.J. Williams, J. Org. Chem., 31, 3032 (1966). We thank Professor Sam Danishefsky for acquainting us with this work and for guiding our thinking about the ketenimine oxidation mechanism.
- 5) This is yet another example of the perfluoroalkyl effect (D.M. Lemal and L.H. Dunlap, Jr., J. Amer. Chem. Soc., 94, 6562 (1972)).
- 6) The reverse reaction, conversion of a furan to a cyclopropenyl ketone (or aldehyde), is common in furan photochemistry, and with  $t$ -butyl-substituted furans the photoisomerization occurs in both directions (E.E. van Tamelen and T.H. Whitesides, J. Amer. Chem. Soc., 93, 6129 (1971); 90, 3894 (1968)). For a recent review, see A. Lablache-Combier in "Photochemistry of Heterocyclic compounds," O. Buchardt, Ed., Wiley, New York, 1976, pp. 136-139.
- 7) Phosphorus pentabromide can be substituted for elemental bromine as the isomerization catalyst. The furan is also formed, albeit not cleanly, when thionyl chloride or phosphorus pentachloride (but not trichloride) are used.
- 8) H.A. Wiebe, S. Braslavsky, and J. Heicklen, Can. J. Chem., 50, 2721 (1972). E.D. Laganis and D.M. Lemal, unpublished results.
- 9) J. Burdon, G.E. Chivers, and J.C. Tatlow, J. Chem. Soc. (C), 2146 (1970); J. Burdon, J.C. Tatlow, and D.F. Thomas, Chem. Commun., 48 (1966).