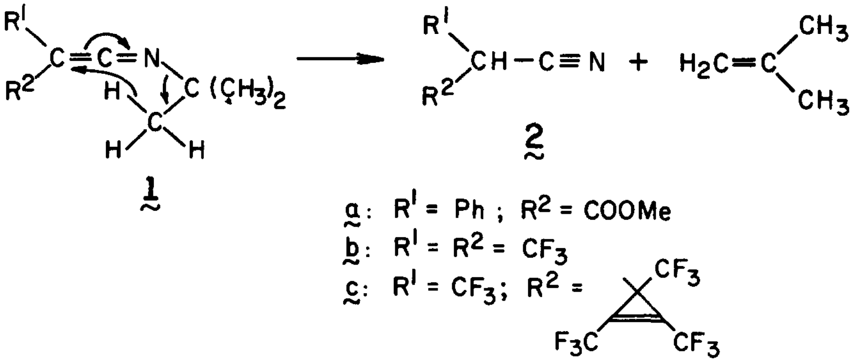
Tetrahedron Letters No.59, pp. 5179-5180, 1969. Pergamon Press. Printed in Great Britain.

THE PYROLYSIS OF KETEN-N-*t*-BUTYLIMINES

Engelbert Ciganek
Central Research Department, E. I. du Pont de Nemours and Company,
Wilmington, Delaware 19898*

(Received in USA 5 November 1969; received in UK for publication 25 November 1969)

We find that pyrolysis of a number of keten-N-*t*-butylimines produces isobutene and a nitrile. Thus, heating a solution of phenylmethoxycarbonylketen-N-*t*-butylimine (**1a**)[1] in deuteriochloroform to 145-160° gives methyl phenylcyanoacetate (**2a**); similarly, keeping a benzene solution of bis(trifluoromethyl)keten-N-*t*-butylimine[2] at 145° for one hour results in complete conversion to isobutene and bis(trifluoromethyl)acetonitrile.[3] Thermal decomposition of (trifluoromethyl)[tris(trifluoromethyl)cyclopropenyl]keten-N-*t*-butylimine (**1c**)[4] in the gas phase at 450° under reduced pressure in a flow system results in formation of 3,3,3-trifluoro-2-[tris(trifluoromethyl)cyclopropenyl]propionitrile (**2c**) in 64% yield; **2c**[5] has b.p. 62° (90 mm); m/e 351; ir max (CCl$_4$) 1905 cm^{-1}; ^{1}H-nmr (neat) quartet at τ 5.9, J = 7 cps; ^{19}F-nmr multiplets of equal intensities at δ + 61.3, 62.0, 69.9 and 70.8 (from external Freon® 11).



---

*Contribution No. 1638.

Preliminary investigations show that the disappearance of **1a** follows first-order kinetics, the reaction **1a** → **2a** having an activation energy of 30 kcal/mole and an activation entropy of -8 e.u. The latter parameter indicates that the reaction is concerted; it could thus be considered to be analogous to the reversal of an ene reaction[6] in which **2** is the ene and isobutene the enophile. Models indicate that a cyclic six-membered transition state as depicted in the scheme is essentially strain free.[7,8]

References

(1) E. Ciganek, J. Org. Chem., in press.

(2) Prepared by reaction of bis(trifluoromethyl)ketene with N-(triphenylphosphoranylidene)-*t*-butylamine.

(3) J. D. LaZerte, U.S. Patent 2,704,769 (1955); C. A. **50**, 2654 (1956).

(4) The ketenimine **1c** is produced on treating hexafluoro-2-butyne with *t*-butyl isocyanide: T. R. Oakes, H. G. David, and F. J. Nagel, J. Am. Chem. Soc., **91**, 4761 (1969). We have independently observed the same reaction.

(5) Satisfactory elemental analysis was obtained for this compound.

(6) H. M. R. Hoffmann, Angew. Chem. **81**, 597 (1969).

(7) Alternatively, a ketenimine $R^1R^2C{=}C{=}NH$ may be formed first *via* a four-membered transition state, followed by a rapid prototropic shift to give **2**.

(8) In analogy to the well-studied thermolysis of keten-N-(cyanoalkyl)-imines[9], the possibility exists that **1** initially cleaves to give the radicals R^1R^2 (NC)C· (A) and Me_3C· (B), followed by disproportionation to **2** and isobutene. However, the complete absence of coupling products (such as A-A or A-B) and of isobutane in the reaction mixture speaks against a radical mechanism.

(9) For a review see H. D. Hartzler, "Chemistry of the Cyano Group", Chapter 11, Z. Rappoport, Ed., Interscience Publishers, London, in press.