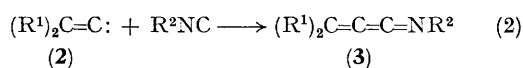
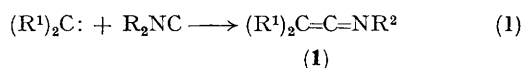


By PETER J. STANG and JON A. BJORK

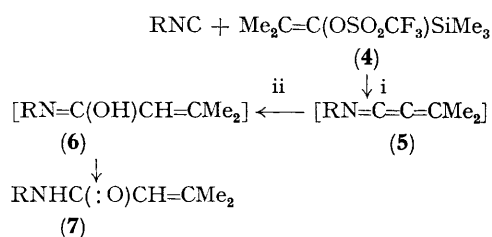
(Department of Chemistry, The University of Utah, Salt Lake City, Utah 84112)

THE reaction of carbenes with isonitriles is known² to give moderate yields of alkenylideneamines (**1**).³ The analogous reaction of alkylidenecarbenes⁴ (**2**) should give alkadienylideneamines (**3**) [reactions (1) and (2)]. In fact,



little is known about this interesting class of heterocumulenes; they have only been reported once⁵ as an intermediate in one reaction. We now report the results of an investigation of the reaction of isopropylidenecarbene (**2**, R¹ = Me) with a variety of isonitriles.

Ethyl-, phenyl-, and 2-ethyl-5-methylphenyl-isocyanides were prepared by standard procedures.⁶ The carbene (**2**) was generated from the silylvinyl trifluoromethanesulphonate (**4**) *via* phase transfer procedures⁷ using stoichiometric amounts of benzyltriocetylammmonium chloride (BTOAC) as the phase transfer agent (see Scheme).



SCHEME. i, KF, BTOAC, H₂O, CH₂Cl₂, 0—5 °C, 20 h; ii, H₂O.
R = Et, Ph, or 2-ethyl-5-methylphenyl.

Under these conditions, 35—52% yields of the appropriately *N*-substituted acrylamides (**7**) were obtained. The acrylamides (**7**) were the sole products observed and were

identified by g.l.c.-co-injection and spectral comparison with authentic samples. Authentic acrylamides (**7**) were prepared by reaction of commercially available 3-methylbut-2-enoic acid with thionyl chloride followed by the appropriate amine.

The acrylamides (**7**) could only come from reaction of the intermediate alkadienylideneamines (**5**) with water as shown, indicating that they are indeed formed in the reaction of unsaturated carbenes with isonitriles. Running the re-

action under anhydrous conditions, with excess of isonitrile as both substrate and solvent, in the presence of (**4**) and using benzyltrimethylammonium fluoride as the carbene initiator⁷ gave no detectable products,† although the starting trifluoromethanesulphonate (**4**) had disappeared.

This research was supported by the Petroleum Research Fund, administered by the American Chemical Society.

(Received, 30th August 1978; Com. 938.)

† Addition of water, after the disappearance of all the carbene precursor (**4**) gave a 3% yield of the acrylamide (**7**) with no other product detectable by g.l.c. Control experiments demonstrated no formation of (**7**), in the absence of (**4**), under the reaction conditions.

¹ Abstracted in part from the M.S. Thesis of J. A. Bjork, The University of Utah, 1978.

² A. Halleaux, *Angew. Chem. Internat. Edn.*, 1964, **3**, 752; J. Boyer and W. Beverung, *Chem. Comm.*, 1969, 1377; J. A. Green and L. A. Singer, *Tetrahedron Letters*, 1969, 5093; N. Obata and T. Takizawa, *ibid.*, p. 3404; E. Ciganek, *J. Org. Chem.*, 1970, **35**, 862.

³ For a review of alkenylideneamines, see: G. R. Krow, *Angew. Chem. Internat. Edn.*, 1971, **10**, 435.

⁴ P. J. Stang, *Accounts Chem. Res.*, 1978, **11**, 107; P. J. Stang, *Chem. Rev.*, 1978, **78**, 383; H. D. Hartzler, in 'Carbenes,' Vol. 2, eds. R. A. Moss and M. Jones, Jr., Wiley-Interscience, New York, 1975.

⁵ H. J. Bestman, G. Schmid, and D. Sandmeier, *Angew. Chem. Internat. Edn.*, 1975, **14**, 53.

⁶ I. Ugi, 'Isonitrile Chemistry,' Academic Press, New York, 1971.

⁷ P. J. Stang and D. P. Fox, *J. Org. Chem.*, 1977, **42**, 1667.