Reaction of Isopropylidenecarbene with Isonitriles. Evidence for the Formation of Alkadienylideneamine¹

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Summary Interaction of alkylidenecarbenes with isonitriles results in vinylamides via the intermediacy of alkadienylideneamines.

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

$$(\mathbf{R}^{1})_{2}\mathbf{C}: + \mathbf{R}_{2}\mathbf{N}\mathbf{C} \longrightarrow (\mathbf{R}^{1})_{2}\mathbf{C}=\mathbf{C}=\mathbf{N}\mathbf{R}^{2}$$
(1)
(1)

$$(\mathbf{R}^{1})_{2}\mathbf{C}=\mathbf{C}: + \mathbf{R}^{2}\mathbf{N}\mathbf{C} \longrightarrow (\mathbf{R}^{1})_{2}\mathbf{C}=\mathbf{C}=\mathbf{C}=\mathbf{N}\mathbf{R}^{2} \qquad (2)$$
(2)
(3)

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, $R^1 = Me$) 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 stoicheiometric amounts of benzyltrioctylammonium 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 reaction 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.

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 \dagger 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. L. Bestman, C. Schmid, condemicat. Angew. Chem. Internat. Edn., 1975, 14, 52

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