

ACCESS TO AMINOPHENYLCARBENES VIA DIAZIRINE EXCHANGE REACTIONS

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Summary. Phenylbromodiazirine (1) reacts with a variety of primary and secondary amines affording a series of aminophenylcarbenes (3).

Aminocarbenes are of interest because the strongly electron-donating amino group should significantly affect their stability and philicity.¹ Several generative methods have been reported for aminocarbenes, including the thermal reversion of formal aminocarbene dimers,² thermal elimination of an amine or alcohol from an amide acetal or related triheteroatomic substituted methane,³ deprotonation of amino-stabilized carbocations,^{3b,4} and the action of carbon atoms on ammonia or amines.⁵ However, excepting a single report of the generation of aminocyanocarbene by pyrolysis or photolysis of a tosylhydrazone salt,⁶ aminocarbenes have not been produced from the classic diazoalkane⁷ or diazirine⁸ carbene precursors. Now we describe reactions of amines with phenylbromodiazirine⁹ that appear to occur by initial exchanges¹⁰ affording aminophenyldiazirines, followed by nitrogen loss and the liberation of aminophenylcarbenes.

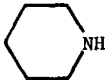

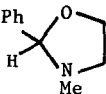
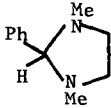
Reactions of phenylbromodiazirine (1) and amines were carried out at 25°C by stirring 1 - 2 mmol of 1 with a 4 - 5 molar excess of amine for 2 (1° amines) or 16 (2° amines) hrs., either in a sealed Carius tube or in a dessicant-protected flask, depending on the volatility of the amine. Reaction products were separated by quenching with 10 ml of aq. 1 M NaOH, followed by extraction with 3 x 10 ml of pentane. Standard manipulations, followed by Kugelrohr distillation and, where appropriate, crystallization, afforded pure products. Table I summarizes the results of six reactions of 1 with various 1° and 2° amines. No reactions were observed between 1 and ammonia or trimethylamine.

Products were identified by comparisons of physical properties, gc retention times, and nmr spectra with those of authentic samples prepared by condensations of the amines with benzaldehyde. References to the authentic compounds appear in the Table.

The most reasonable mechanism to account for the reactions of Table I posits an initial amine/bromide exchange¹⁰ of 1, affording an unstable aminophenyldiazirine, 2, that yields aminophenylcarbene 3 upon loss of nitrogen, eq. (1). In Cases 1 and 2 of Table I, where R' = H, 3 affords an imine, probably by 1,2 N→C H migration. In contrast, when R = R' = alkyl (Cases 3 and 4), 3 attacks a second amine molecule, providing a (formal) N-H insertion product.

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Table I. Reaction Products from Phenylbromodiazirine and Amines

Case	Reactant amine	Product	Isolated yield (%)	Reference ^a
1	MeNH ₂	PhCH=NMe	71	b
2	H ₂ NCH ₂ CH ₂ NH ₂	(PhCH=NCH ₂ -) ₂	66	c
3	Me ₂ NH	PhCH(NMe ₂) ₂	83	d
4		PhCH(N  ₂) ₂	58	e
5	MeNHCH ₂ CH ₂ OH		59	f
6	MeNHCH ₂ CH ₂ NHMe		72	f

^aReferences are to authentic products.

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- (16) PhCNMe_2 may be an ambiphile because $1.5 < m < 2.2$; cf., ref. 1, Moss.

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