Methoxyphenyldiazirine as Precursor to Methoxyphenylcarbene

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Reaction of bromo(phenyl)diazirine (2) with methoxide ion gives methoxy(phenyl)diazirine (3), which yields
cyclopropanes (4) on photolysis in alkenes.

Methoxyphenylcarbene (1) is well known in its metal–carbene
complex form. Cyclopropanations of electron-deficient
alkenes have been achieved upon thermolyses of the penta-
carbonyl Cr, Mo, and W carbene complexes; although mechan-
istic studies suggest that these cyclopropanations occur by
ligand transfer within carbene–alkene–metal complexes, not
via the free carbene.[1]

The chemistry of the free carbene is problematical. Pyrolyses
of the Na (or K) salt of PhC(OMe)=N–NHSO$_2$C$_6$H$_4$Me-*p* gave
mainly PhC(OMe)=N–N=C(OMe)Ph.[2] Cyclopropanes could
not be isolated from similar pyrolyses in the presence of
keten dialkylacetal or cyclohexene carbene traps,[2,3] although
pyrolysis in dec-1-ene afforded 4% of 1-methoxy-1-phenyl-2-
n-octylcyclopropane isomers.[3] On the other hand, cyclopro-
panation of dialkyl fumarates occurred readily on thermolysis
in the presence of PhC(OMe)=N–NHSO$_2$C$_6$H$_4$Me-*p* salts[3] or
of α,α-dimethoxybenzyltriphenylsilane.[4] More recently, pyro-
lysis of PhC(OMe)=N–N=PPh$_3$ was shown to afford a com-
plicated product mixture attributed to the carbene (1).[5]

We now report an unprecedented reaction of bromo-
(phenyl)diazirine (2)[6] with methoxide ion, which affords
methoxy(phenyl)diazirine (3); the latter yields cyclopropanes
(4) upon photolysis in simple alkenes (Scheme 1).

A solution of (2) (10 mmol) in dimethylacetamide (2 ml) was
slowly added to a mechanically stirred solution of NaOMe (22
mmol) in dimethylacetamide–hexamethylphosphoric triamide
(30 ml; 1:1; DMA-HMPT) at −10 °C. After 1 h of stirring
at −10 °C, the yellow-green methoxy(phenyl)diazirine (3) was
obtained by pentane extraction (3 × 50 ml), drying (MgSO$_4$),
and concentration *in vacuo* (−10 °C) to 5 ml.† The i.r.
spectrum (film, precooled plate) of a concentrated solution of
(3) revealed a band at 1570 cm^{-1} (N=N), similar to those for
(2) (1555 cm^{-1}) and chloro(phenyl)diazirine (1560 cm^{-1});[6] the
2000—2400 cm^{-1} region was blank, demonstrating the absence
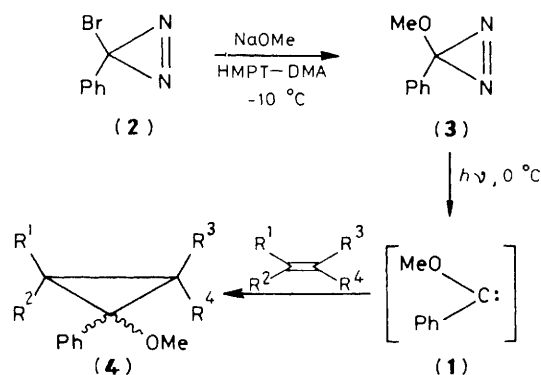
Scheme 1

|	R^1	R^2	R^3	R^4
a;	Me	Me	H	H
b;	Me	H	H	Me
c;	Me	Me	Me	H
d;	Me	Me	Me	Me

of a diazoalkane. Its n.m.r. spectrum (CDCl$_3$; −10 °C; Me$_4$Si
ref.) showed MeO (δ 3.28) and aromatic resonances. Its u.v.
spectrum (−30 °C; pentane) revealed maxima at 368 and
383 nm, with significant, though decreasing, absorption at
ca. 450 nm. Sample instability prevented an accurate deter-
mination of ε values. Chloro- and bromo-(phenyl)diazirines are
reported to exhibit 'broad' u.v. absorptions with λ$_{max}$ 388 nm.[6]

Photolysis (G. E. Sunlamp; Pyrex tube; 0 °C; 3 h) of (3) in
ethanol gave benzaldehyde ethyl methyl acetal (5) in 26%
yield based on the diazirine (2). Gas chromatography on SE-30
at 115 °C gave a pure sample‡ with a definitive n.m.r. spec-
trum. Reaction of the carbene (1) with methanol affords
benzaldehyde dimethyl acetal, an analogue of (5).[2]

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† The diazirine (3) is thermally and photochemically unstable; all
operations must be performed at <0 °C and in dim light. Reac-
tions of (3) employed the concentrated pentane extract.

‡ A satisfactory elemental analysis was obtained.

Similar photolyses of (3) in isobutene, *trans*-but-2-ene, and trimethylethylene afforded the cyclopropanes (4a—c)‡ in 12, 7, and 15% yields, respectively, based on (2); Scheme 1. Although the yields are low, cyclopropanes were the major volatile

$$\text{PhCH(OMe)(OEt)} \qquad \text{PhCH(OMe)C(Me}_2\text{)C(Me)=CH}_2$$
$$\text{(5)} \qquad\qquad\qquad\qquad \text{(6)}$$
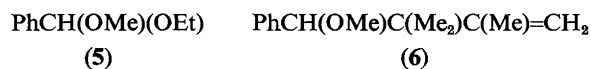
products in all cases,§ and were readily purified by g.c. Structures were established by elemental analysis and n.m.r. spectroscopy. The cyclopropane (4a), for example, showed δ (CCl$_4$; Me$_4$Si) 0.72 (s, 3H, CMe), 0.52, 0.62, and 0.83, 0.93 (AB q, J 6 Hz, 2H, CH$_2$), 1.30 (s, 3H, CMe), 3.07 (s, 3H, OMe), and 7.33 ('s', 5H, Ph). Reaction with tetramethylethylene did not afford the expected cyclopropane (4d). Instead, g.c. isolation (SE-30; 140 °C) gave a product tentatively assigned the alkene structure (6), which can be construed as a rearrangement product of (4d). The n.m.r. spectrum of the initial photolysis product indicated that (6) was already the major constituent; little (4d) could have been present.

There is direct spectroscopic evidence for formation of chlorophenylcarbene upon photolysis of phenylchlorodiazirine,[8] so that it is reasonable to suggest that photolysis of

(3) affords the carbene (1), the proximate precursor of the cyclopropanes (4). The mechanism of the conversion of the bromodiazirine (2) into the methoxydiazirine (3), however, is obscure. A simple S_N1 process would require the intermediacy of a high-energy[9] (phenyl)diazirinium cation. Though postulated,[6] diazirinium ions have thus far eluded experimental detection.[10] A pathway involving an intimate diazirinium cation–bromide ion pair is most likely for this unusual conversion.

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§ Identified volatile side products [yields based on (2) for the reaction with isobutene] included benzaldehyde (2%), benzaldehyde dimethyl acetal (5%), and methyl benzoate (<1%); these are attributable to reactions of (1).[2,3,5] The phenylbromocarbene adduct of isobutene was absent (n.m.r.).[7] Non-volatile side products included PhC(OMe)=N–N=C(OMe)Ph (1%)[8] and the formal dimers of (1) (<1%).

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