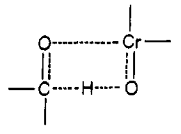
J. Org. Chem. 1988, 53, 2159–2162



I

Acknowledgment. The financial support to the project by UGC and CSIR, India, is gratefully acknowledged.

Registry No. $PhCH_2OH$, 100-51-6; 4-$HOCH_2C_6H_4Me$, 589-18-4; 4-$HOCH_2C_6H_4OMe$, 105-13-5; 4-$HOCH_2C_6H_4NHCOMe$, 16375-88-5; 4-$HOCH_2C_6H_4SMe$, 3446-90-0; 4-$HOCH_2C_6H_4F$, 459-56-3; 4-$HOCH_2C_6H_4CO_2Me$, 6908-41-4; 4-$HOCH_2C_6H_4Cl$, 873-76-7; 4-$HOCH_2C_6H_4CF_3$, 349-95-1; 4-$HOCH_2C_6H_4NO_2$, 619-73-8; 3-$HOCH_2C_6H_4Me$, 587-03-1; 3-$HOCH_2C_6H_4F$, 456-47-3; 3-$HOCH_2C_6H_4Br$, 15852-73-0; 3-$HOCH_2C_6H_4OMe$, 6971-51-3; 3-$HOCH_2C_6H_4OPh$, 13826-35-2; 3-$HOCH_2C_6H_4CN$, 874-97-5; 3-$HOCH_2C_6H_4SMe$, 59083-33-9; 3-$HOCH_2C_6H_4CF_3$, 349-75-7; 3-$HOCH_2C_6H_4NO_2$, 619-25-0; 3-$HOCH_2C_6H_4NHCOMe$, 16375-94-3; 2-$HOCH_2C_6H_4Me$, 89-95-2; 2-$HOCH_2C_6H_4F$, 446-51-5; 2-$HOCH_2C_6H_4Cl$, 17849-38-6; 2-$HOCH_2C_6H_4Br$, 18982-54-2; 2-$HOCH_2C_6H_4NO_2$, 612-25-9; 2-$HOCH_2C_6H_4NHCOMe$, 20939-77-9; 2-$HOCH_2C_6H_4I$, 5159-41-1; 2-$HOCH_2C_6H_4CF_3$, 346-06-5; 2-$HOCH_2C_6H_4SMe$, 33384-77-9; 2-$HOCH_2C_6H_4OMe$, 612-16-8; D_2, 7782-39-0; pyridinium fluorochromate, 83042-08-4.

β-Cyclodextrin as a Molecular Reaction Vessel: Reactions of Included Phenylmethyldiazirine

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Phenylmethyldiazirine forms a stable, solid complex with β-cyclodextrin. The diazirine was decomposed by pyrolysis or irradiation of the complex, and the reaction products were analyzed. The major volatile products consist of the isomeric 1,2-diphenyl-1-methylcyclopropanes. Under photolytic conditions a significant amount of styrene also is formed. The selectivity for trans isomer formation is 10 times greater from the CD complex than from the neat state. Carbene insertion products with β-cyclodextrin are formed under both reaction conditions. The product distributions are explained by cage and shape-selective effects exerted by β-cyclodextrin.

The cyclodextrins (CD's) are a series of cyclic oligosaccharides which possess a hydrophobic pocket.[1] Their inclusion complexes with lipophilic molecules, especially aromatic compounds, have been studied thoroughly. The interest in CD's derives in part from their similarity to enzymes, and recent effort has been put into modifying cyclodextrins to enhance their catalytic powers.[2] Cyclodextrins also have been used to control photoreactions of bound guests.[3] However, few studies report the chemistry of thermally generated reactive intermediates inside the cyclodextrin cavity.

Ramamurthy, Turro, and co-workers have found that cyclodextrins exert "super cage" effects and conformational effects in certain ketone photoreactions.[3] Cage effects result in the preference for direct coupling products over escape products from radical pairs. They are typically demonstrated by using a precursor to an unsymmetrical radical pair (A$^\bullet$ $^\bullet$B). Symmetrical products (A–A and B–B) are produced from coupling of escaped radicals, whereas unsymmetrical products (A–B) result from both direct coupling and from coupling of escaped radicals. The cage effect exerted by cyclodextrins on ketone cleavage photoreactions was shown by using unsymmetrical dibenzyl ketones and benzyl phenylacetates; both predominantly produce unsymmetrical 1,2-diphenylethanes by direct coupling of the benzyl–benzyl radical pair produced via loss of CO and CO_2, respectively.[4] Conformational effects can result in selectivity for one reaction pathway over another, especially when at least one pathway is conformationally dependent. For instance, type I and type II reactions are often competing pathways in the photochemistry of ketones. Cyclodextrin complexation has altered the reactivity to favor either pathway. Benzoin alkyl ethers, which react via α-cleavage in solution, selectively undergo type II reactions in the cyclodextrin complex.[5] On the other hand, α-alkyl dibenzyl ketones undergo type I reactions while included into cyclodextrin, whereas both reactions occur in solution.[3] These disparate results can be understood based on the geometry of the inclusion complex. In the benzoin alkyl ether complex the ether chain is not bound by the cavity, so it can participate in the type II process. In the α-alkyl dibenzyl ketone complex, however, the alkyl chain is buried inside the cavity and therefore not accessible to the carbonyl oxygen.

Cyclodextrins have been used to influence many thermal reactions. However, they have rarely been used as a medium for thermally generating very reactive intermediates. The pyrolysis of azobisisobutyronitrile (AIBN) as the solid complex with β-cyclodextrin is an example of thermal generation of a radical pair. The radical pair produced after nitrogen extrusion undergoes recombination; it behaves like the radical pairs generated from ketone photolysis.[3] Again, the cyclodextrin appears to enhance the cage effect, although in this case the escape products and the coupling products would be identical. Only one example of carbene generation inside a CD has been found.[6]

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(1) Bender, M. L.; Komiyama, M. *Cyclodextrin Chemistry*; Springer-Verlag: New York, 1978. Saenger, W. *Angew Chem., Int. Ed. Engl.* **1980**, *19*, 344.

(2) Breslow, R. *Science (Washington, D.C.)* **1982**, *218*, 532. Tabushi, I. *Acc. Chem. Res.* **1982**, *15*, 66. D'Souza, V. T.; Bender, M. L. *Acc. Chem. Res.* **1987**, *20*, 146.

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0022-3263/88/1953-2159$01.50/0

Table I. Pyrolysis Products of 1 and 1•β-CD

		% rel compstn			product ratios[a]			
substrate	conditions	4	5	3	4/5	(4 + 5)/3	% other products	% yield
1·β-CD	200 °C, 0.2 mm	87	4	9	25	9	<3	53
1·β-CD	200 °C, N_2	86	5	9	18	10	17[b]	42
1·β-CD	130 °C, Ar	84	4	12	24	7	15[b]	66
1·β-CD	75 °C, 0.2 mm	72	4	24	18	3	13[c]	32
1	200 °C, Ar	*d*	*d*	*d*			>97[e]	>95
1	130 °C, Ar	20	8	72	2.6	0.4	15[b]	60
2 + 7	100 °C, N_2	66	27	7	2.4	14	<3	74

[a] Calculated from the experimental data; calculation using the relative composition may give different values. [b] Acetophenone is the major other product. [c] 3,3-Diphenyl-2-butanone is the major other product. [d] Too small to determine. [e] Styrene is the major product; see Experimental Section for special reaction conditions.

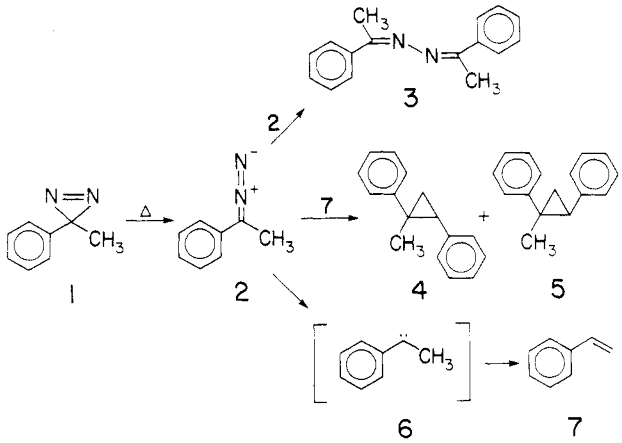
In that study dichlorocarbene was formed in solution by deprotonation of chloroform followed by chloride elimination from the resultant trichloromethyl anion. If phenoxide anion is present (Reimer–Tiemann reaction), then it normally reacts with the carbene at the ortho and para positions, and a mixture of *o*- and *p*-hydroxybenzaldehydes is produced after hydrolytic workup. In the presence of α- and β-CD the Reimer–Tiemann reaction shows a selectivity for *p*-hydroxybenzaldehyde formation. The authors proposed that dichlorocarbene is formed inside the CD cavity; thus, the para position selectively undergoes reaction because the phenolate ion enters the CD with the oxygen directed away from the cavity. No reaction of the carbene with the CD was found. Dichlorocarbene, of course, cannot be considered a "very" reactive intermediate, as shown in part by its selective reactivity. To our knowledge, no carbene reactions in solid CD-complexes have been studied.

In this paper we explore the effect of cyclodextrin complexation on the decomposition of phenylmethyldiazirine (**1**). The thermal and photochemical degradation of **1** has been investigated thoroughly by Liu and co-workers (Scheme I).[7] Thermolysis of **1** is thought to result in ring opening to phenyldiazoethane (**2**). The major product, acetophenone azine (**3**), results from bimolecular reaction of **2** (or from bimolecular reactions involving carbene **6**), whereas the isomeric diphenylmethylcyclopropanes **4** and **5** are formed by reaction of **2** with styrene (**7**). Styrene is produced from **2** after nitrogen extrusion and subsequent 1,2-hydrogen shift in carbene **6**.[8] Photochemical decomposition can lead to different product distributions. For example, the diazirine can suffer direct nitrogen loss as well as isomerization to the linear diazo compound. Photolytic reactions often give rise to intermediates or products with an excess of internal energy, and they introduce the possibility of triplet state reactions. With arylalkyldiazirines rearrangement to the diazo compound appears to dominate over direct nitrogen extrusion.[7] Direct irradiation of **2** in solutions gives mainly azine, even in an excess of an olefin trap.[9]

Experimental Section

NMR spectra were recorded on a Varian FT-80A spectrometer. Gas chromatography was performed on a Hewlett-Packard 5790A instrument using a 23-m capillary column of 5% phenylmethyl silicone and an FID detector. Absorption measurements were obtained with a Beckman Acta V spectrometer. β-Cyclodextrin was used as obtained from Aldrich, except in UV studies where it was recrystallized from H_2O.

Scheme I



Binding Constant. A Benesi–Hilderbrand[10] plot was generated by measuring the absorbance at 218 nm of solutions containing 1 mL of a 9.1×10^{-5} M methanol solution of phenylmethyldiazirine which was diluted to 10 mL with an aqueous β-cyclodextrin solution. Owing to the relatively small $\Delta\epsilon$ ($\Delta\epsilon/\epsilon \leq 0.07$) and the mixed solvent system, the calculated binding constant of 4×10^2 M^{-1} is at best an order of magnitude approximation.

Preparation of the β-CD Complex of 1. Phenylmethyldiazirine was made by the method of Liu et al.[7] The *N*-benzylimine of acetophenone was reacted with hydroxylamine-*O*-sulfonic acid in methanolic ammonia to produce the diaziridine. Oxidation of the diaziridine with Ag_2O gave the diazirine, which was purified by chromatography (SiO_2, pentane). The complex was made by adding the neat diazirine to a 0.02 M aqueous β-cyclodextrin solution (1.0–1.2:1 β-CD/$C_8H_8N_2$) and stirring vigorously overnight under N_2. The resulting precipitate was isolated by filtration and washed with H_2O. The wet paste was transferred to a flask and was dried in vacuo (0.05 Torr) overnight. Yields ranged from 68% to 72%. The ratio of β-cyclodextrin to **1** in the solid was determined spectrometrically by NMR integration and gravimetrically by reisolation or by derivatization. The diazirine was reisolated by dissolving the complex in H_2O and extracting several times with Et_2O. The 1-phenylethyl acetate derivative of **1** was made by consuming the complex in boiling CH_3CO_2H for 1 h. Ratios were in the range 1:0.9–1.2 β-CD/**1**. The complex showed no detectable decomposition by NMR after storage in a refrigerator for several weeks.

Pyrolysis of the CD Complex. A quantity (1.0–2.0 g) of the complex in a flask under vacuum or an inert atmosphere was

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(6) Komiyama, M.; Hirai, H. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2053. Komiyama, M.; Hirai, H. *Makromol. Chem., Rapid Commun.* **1981**, *2*, 707. Ohara, M.; Fukuda, J. *Pharmazie* **1978**, *33*, 467.

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Table II. Photolysis Products from 1 and 1•β-CD

		% rel compstn				product ratios[a]			
substrate	conditions	4	5	3	7	4/5	(4 + 5 + 7)/3	% other products	% yield
1·β-CD	30 °C, 0.5 mm	40	8	15	37	5	6	25[b]	51
1	30 °C, N_2	14	14	70	2	1	0.4	25[c]	96
1·β-CD	30 °C, H_2O[d]	54	46	*e*	*e*	1		86[f]	76

[a] Calculated from the experimental data; calculation using the relative composition may give different values. [b] 3,3-Diphenyl-2-butanone is the major other product. [c] Acetophenone and *trans*-1,2-dimethylstilbene are the major other products. [d] Irradiated as a slurry in water. [e] Too small to measure. [f] 1-Phenylethanol is the major product.

immersed into an oil bath which was held at a given temperature (75–200 °C). At high temperatures a purple coloration was generated transiently. After decomposition was complete, the residue was dissolved in H_2O, and the aqueous layer was extracted 3× with Et_2O. The combined organics were dried and concentrated in vacuo. The residue was dissolved in CH_2Cl_2, and the solution was filtered through a plug of SiO_2. The filtrate was analyzed by GC. Results and conditions are presented in Table I. The β-CD derivatives were isolated after concentrating the aqueous layer in vacuo and subjecting the residue to flash reverse-phase chromatography (J. T. Baker, C-18) using a gradient elution (0–40% CH_3CH/H_2O). The *O*-(1-PhEt)-β-CD containing fractions were combined and concentrated in vacuo. TLC (Baker Si250F, 5:4:3 *n*-BuOH/EtOH/H_2O) showed at least two spots, R_f 0.62 and 0.75. Yields ranged from 36% to 44% based on β-CD. ^1H NMR (D_2O, 68 °C, 3-(trimethylsilyl)propanoate-d_4, δ) showed two aromatic [7.5, 7.3 (br s's)], a benzylic ether [4.5 (br q, *J* = 7 Hz, obscured by H_2O], and two methyl resonances [1.5, 1.4 (br d's, *J*'s = 7 Hz)] along with the expected cyclodextrin signals.

Photolysis of CD Complex. The complex was placed in a Pyrex round-bottom flask and irradiated under vacuum or an inert atmosphere with a Hanovia 450-W medium-pressure lamp for 8–16 h. The flask was rotated constantly by using a rotary evaporator motor and immersed in a water-cooled water bath to minimize heating of the complex (bath temperature 28–32 °C). The resulting solid was then worked up as above. The results are presented in Table II. The *O*-(1-PhEt)-β-CD derivatives were isolated in 33% yield. One solution-phase photolysis of the complex was tried. The complex (0.6 g) was slurried in H_2O (970 mL) and irradiated as above for 3.5 h. The main product isolated as above was 1-phenylethanol. No β-CD insertion products were formed.

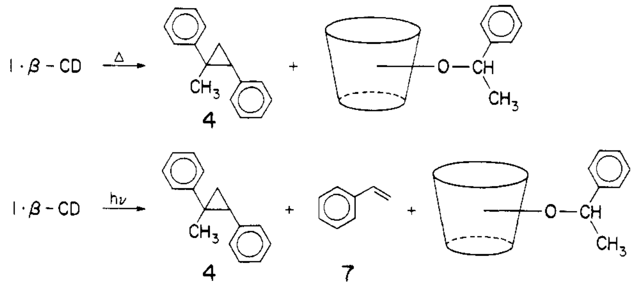
Control Reactions. The neat diazirine was decomposed under conditions similar to those used to decompose the diazirine/β-CD complex. The diazirine was pyrolyzed at 200 °C by slow dropwise addition to the heated flask (immersion of the entire sample results in violent evolution of N_2!). At this temperature the diazirine and/or the resulting styrene volatilize so that intermolecular products are not obtained. In contrast, at 130 °C the entire sample can be immersed, and the mixture "refluxed". Control reaction results are presented in Tables I and II.

Reaction Products. Volatile products isolated by extraction of the spent cyclodextrin complex were synthesized independently for comparison by GC and NMR. The 1,2-diphenyl-1-methylcyclopropanes[7] were made by thermal decomposition of phenyldiazoethane[11] (0.80 g, 6.1 mmol) in 18 mL of styrene (Aldrich) at 100 °C and purified by distillation (0.89 g, 4.3 mmol, 71%). Acetophenone azine was made from reaction of acetophenone (Mallinckrodt) with hydrazine hydrate and purified by recrystallization.[12] The dimethylstilbenes were made from $TiCl_3$–$LiAlH_4$-induced reductive coupling of acetophenone and purified through chromatography (SiO_2, hexane) followed by distillation.[13] 3,3-Diphenyl-2-butanone was made by pinacol rearrangement of 2,3-diphenylbutane-2,3-diol (Aldrich) and purified by distillation.[14]

Results

Treatment of an aqueous β-CD solution with an equimolar amount of 1 precipitates a stable 1:1 complex.[15] Although the structure of the complex was not determined experimentally, several results support an inclusion structure. The complex does not dissociate when heated to 200 °C under vacuum (vide supra). A significant shape selectivity is indicated in the reaction products. A binding constant for complex formation was obtained which is consistent with other similar compounds known to bind via inclusion. Finally, substituted benzenes are well-known to form inclusion complexes where the guest resides in the cavity in the solid state.[1,3,16]

Photolytic or pyrolytic decomposition of the diazirine complex results in roughly equal distribution of extractable, volatile products and CD-insertion products. The volatile products' distribution differs dramatically from that produced by neat diazirine decomposition (Table I). The largest effect is seen with the ratio of *trans*- to *cis*-1,2-diphenyl-1-methylcyclopropane. In the absence of cyclodextrin the ratio is about 2.5:1, whereas decomposition of the CD complex results in a ratio as large as 25:1. Also different is the ratio of azine to the purely hydrocarbon products, **4**, **5**, and styrene. Neat diazirine decomposition produces mainly azine, whereas the CD complex decomposes to produce mainly hydrocarbons. The pyrolytic and photolytic decomposition products differ in several respects. Most dramatic is the isolation of a significant amount of styrene under photolytic conditions; very little styrene is recovered from pyrolysis runs.



Carbene insertion products with β-CD are also formed both thermally and photochemically. They were separated from unreacted β-CD by flash reverse-phase chromatography. TLC indicated the presence of at least two derivatized β-CD's. The crude structure of these adducts was assigned based on ^1H NMR. Methyl doublets near 1.4 ppm and a methine quartet at 4.50 ppm are consistent with *O*-1-phenylethyl substitution. Insertion in an O–H bond is certainly expected with a carbene intermediate.[17] Complete separation and characterization of these insertion products and those obtained by decomposition of

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[11] Phenyldiazoethane was prepared by vacuum pyrolysis of the tosylhydrazone sodium salt. See: Creary, X. *Orgn. Synth.* **1985**, *64*, 207. Farnum, D. G. *J. Org. Chem.* **1963**, *28*, 870.

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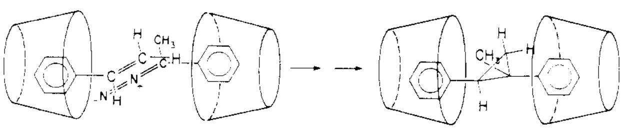
[14] Sisido, K.; Nozaki, H. *J. Am. Chem. Soc.* **1948**, *70*, 776.

[15] Not surprisingly, the corresponding adducts between diazo compounds and β-CD could not be formed without substantial decomposition: Abelt, C. J.; Pleier, J. M., unpublished results.

[16] Le Bas, G.; Tscoucaris, G. *Mol. Cryst. Liq. Cryst.* **1986**, *137*, 287.

[17] Kirmse, W. *Carbene Chemistry*, 2nd ed.; Academic: New York, 1971; Chapter 11.

Scheme II



other diazirine/β-CD complexes will be the subject of a later paper.

Discussion

The β-CD host appears to influence the decomposition of the diazirine guest in two major ways. First, of the several reactions involved in making the final products, the CD causes certain intramolecular pathways to be favored over the bimolecular reactions which dominate during decomposition in solution or the neat state. When 1 is completely isolated (e.g., in the gas phase or in a low-temperature, inert gas matrix), it decomposes to styrene by intramolecular reactions: expulsion of nitrogen and a H-shift. In solution 1 forms azine via bimolecular reactions. Since the formation of 4 and 5 requires the prior production of styrene, the preponderance of these products indicates that the intramolecular formation of styrene is enhanced *relative* to other processes. This intramolecular pathway does not compete effectively with all bimolecular reactions. Azine and cyclopropane formation both occur via bimolecular reactions, but those leading to azine appear to be repressed, while those which give rise to 4 and 5 seem relatively enhanced. One explanation for this disparity is based on the limited lifetime of phenyldiazoethane at high temperatures. The probability for the existence of adjacent phenyldiazoethane molecules, the requirement for reaction in the solid state, is small. The requirement for cyclopropane formation is easier to satisfy: phenyldiazoethane needs only to be generated next to a molecule of styrene whose presence is not lifetime limited. This explanation is not completely satisfying, since azine production still dominates even in 0.6% solutions of 2 at elevated temperatures.[7] One intriguing explanation for the preference for cyclopropane products involves the organizing capability of the CD. It is possible that the CD might favorably align styrene and the diazo compound for a 1,3-dipolar cycloaddition (Scheme II). The displayed geometry is consistent with frontier molecular orbital considerations which predict that the most favorable orbital interactions are between the β-carbon of styrene and the diazo group carbon and between the α-carbon of styrene and the terminal diazo nitrogen.[18]

In contrast to the thermal decomposition of 1 in the CD complex, a significant amount of styrene is actually isolated by photochemical degradation. This result might reflect the different diazo compound/carbene distribution and different internal energies (e.g., a "hot" carbene) which are produced by irradiation in the solid state. Yet, 1 gives mainly azine when irradiated as the neat liquid, which indicates that irradiation serves to induce diazo compound formation. Since cyclopropane formation proceeds via a thermally activated cycloaddition, the reaction may be slower in the photolysis procedure due to the lower reaction temperatures. The isolation of styrene makes the β-CD "reaction vessel" effect especially evident in the photolytic decomposition of 1.

The β-CD host also appears to exert shape-selectivity on the cyclopropane products. A dramatic increase in the preference for trans isomer production is observed from the CD-complex compared to the neat liquid. This preference might result from the guest axial inclusion geometry. If the phenyl groups remain roughly aligned axially in the CD cavity, then the bimolecular reaction of styrene with phenyldiazoethane would leave the phenyl groups directed away from each other, and thus trans, in the product (Scheme II). There appears to be a smaller preference for 4 from photolysis. This result might reflect reduced guest movement inside the CD cavity at lower temperatures. Included 1 probably occupies a variety of "sites" in the solid complex. Photolysis at lower temperature produces reactive species in these relatively unequilibrated sites, whereas at higher temperatures the guest molecules can undergo rapid realignment which might favor the trans orientation.

We are continuing to explore the interaction of CD's with bound reactive intermediates with the hope of determining how CD's can be used to control reactivity.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

Registry No. 1, 63269-86-3; 1·β-CD 1:1 complex, 113779-37-6; 2, 22293-10-3; 3, 729-43-1; 4, 14161-73-0; 5, 14161-72-9; 7, 100-42-5; $PhCH_2N{=}C(Ph)CH_3$, 14428-98-9; H_2NOSO_3H, 2950-43-8; 3-methyl-3-phenyldiaziridine, 90006-76-1.

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(18) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: New York, 1976. Hegarty, A. F. In *The Chemistry of the Diazonium and Diazo Groups*; Patai, S., Ed.; Wiley: New York, 1978; Part 2, p 580.