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Generation, Detection, and Reaction of Ammonium Ylides in Reactions of [2-(Dimethylamino)alkyl]phenylcarbenes[†]

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Generation of diphenylcarbene (DPC) bearing a 2-(*N,N*-dimethylamino)methyl group in CHCl$_3$ produced (*N,N*-dimethylamino)phenylisoindolium chloride and dichlorocarbene, which was trapped by added cyclohexene, while DPC having a 2-(*N,N*-dimethylamino)ethyl group afforded not only 3-phenyl-4-(*N,N*-dimethylamino)indane but also 2-[2-(*N,N*-dimethylamino)benzyl]styrene.

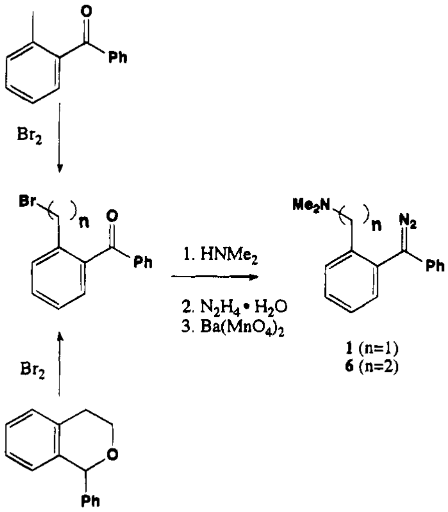
Reactions of carbenes bearing functionalized groups are of interest from both synthetic and mechanistic standpoints.[1] For instance, arylcarbenes that have appropriate alkyl substituents at the 2-position usually react with proximate C−H bonds to form benzocyclic compounds,[2] while those having phenyl[3] and alkenyl[4] groups produce polycyclic compounds as a result of addition to the unsaturated bonds. On the other hand, carbenes having heteroalkyl substituents at the 2-position react with the unshared electron pairs of the heteroatoms to generate ylidic intermediates, which ultimately lead to the final functionalized products.[5,6] These reactions have provided useful information concerning the mechanism of C−H insertion, the role of ylidic intermediates in the reaction, and the proximity effect on the reactivities of carbenes.

In the present work, we generated diphenylcarbenes bearing a series of (dimethylamino)alkyl groups at the ortho position and studied their reactivities in order to learn the effect of structure on the reaction patterns. An ammonium ylide, generated as a result of intramolecular interaction between the carbenic center and the proximate amine nitrogen, was detected spectroscopically and was shown to play a crucial role in the reaction course.

Results and Discussion

The precursor diazo compounds **1** and **6** employed in this study were prepared, as outlined in Scheme 1 as unstable red oils, which were immediately used for photolysis studies without further purification. Key intermediates in the synthesis of **1** and **6** were 2-(bromomethyl)- and 2-(bromoethyl)benzophenones, which were conveniently prepared from 2-methylbenzophenone and 1-phenylisocroman, respectively.

Scheme 1



Irradiation of [2-[(*N,N*-dimethylamino)methyl]phenyl]-phenyldiazomethane (**1**) in degassed methanol solution at 10 °C with a 300 W high-pressure Hg lamp, through a Pyrex filter, produced [2-[(dimethylamino)methyl]phenyl]phenylmethyl methyl ether as the sole isolable product in 90% yield. Formation of the methyl ether can be explained in terms of insertion of the photolytically generated carbene (**2**) into an OH bond of the alcohol (Scheme 2).[7] Similar irradiation of **1** in a nonhydroxylic solvent (e.g., benzene) gave a complex reaction mixture from which a small amount of [2-formylphenyl]- and [2-[(dimethylamino)methyl]phenyl]phenylmethane was isolated by preparative TLC. Monitoring the irradiation of **1** in C$_6$D$_6$ by ^{1}H NMR also showed no signals ascribable to major products. However, similar ^{1}H NMR monitoring of the photolysis of **1** in CDCl$_3$ showed the accumulation of a single major component (~80%) concomitant with disappearance of **1**. Notable changes in the spectrum were that the singlet *N*-methyl signals at 2.19 ppm in **1** were split into two singlets at 3.86 and 2.97 ppm and that the singlet benzylmethylene signals at 3.40 ppm were converted into an AB quartet at 5.35 and 5.16 ppm.

[†] Dedicated to Professer Charles W. Jefford on the occasion of his 65th birthday.

[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1995.

(1) For general reviews, see: (a) Moss, R. A., Jones, M., Jr., Eds. *Carbenes*; Wiley: New York, 1973, 1975; Vols. 1 and 2. (b) Kirmse, W. *Carbene Chemistry*; Academic Press: New York, 1971. (c) Regitz, M., Ed. *Methoden der Organischen Chemie (Houben-Weyl)*; Thieme: Stuttgart, 1989; Vol. E19b.

(2) Gutsche, C. D.; Bachman, G. L.; Udell, W.; Bauerlein, S. *J. Am. Chem. Soc.* **1971**, *93*, 5172. Baer, T. A.; Gutsche, C. D. *J. Am. Chem. Soc.* **1971**, *93*, 5180. Hirai, K.; Komatsu, K.; Tomioka, H. *Chem. Lett.* **1994**, *503*. Tomioka, H.; Okada, H.; Watanabe, T.; Hirai, K. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 873.

(3) Denny, D. B.; Klemchuk, P. P. *J. Am. Chem. Soc.* **1958**, *80*, 3289. Palik, E. C.; Platz, M. S. *J. Org. Chem.* **1983**, *48*, 963. Kirmse, W.; Kund, K.; Ritter, E.; Dorigo, A. E.; Houk, K. N. *J. Am. Chem. Soc.* **1986**, *108*, 6045.

(4) Homberger, G.; Dorigo, A. E.; Kirmse, W.; Houk, K. N. *J. Am. Chem. Soc.* **1989**, *111*, 475.

(5) (a) Kirmse, W.; Kund, K. *J. Am. Chem. Soc.* **1989**, *111*, 1465. (b) Tomioka, H.; Kobayashi, N.; Murata, S.; Ohtawa, Y. *J. Am. Chem. Soc.* **1991**, *113*, 8771.

(6) See for general reviews on ylide chemistry: (a) Johnson, A. W. *Ylid Chemistry*; Academic Press: New York, 1966. (b) Maercker, H. J. *Org. React.* **1965**, *14*, 270. (c) Zugravescu, I.; Petrovanu, M. *N-Ylide Chemistry*; McGraw-Hill: New York, 1976. (d) Nikolaev, V. A.; Korobitsyna, I. K. *Mendeleev Chem. J.* (Engl. Transl.) **1979**, *24*, 88. (e) Ando, W. *Acc. Chem. Res.* **1977**, *10*, 179. (f) Padwa, A.; Hornbuckle, S. F. *Chem. Rev.* **1991**, *91*, 263.

(7) For a review, see: Kirmse, W. In *Advances in Carbene Chemistry*; Brinker, U. H., Ed.; JAI Press: Greenwich, CT, 1994; Vol. 1, pp 1−57.

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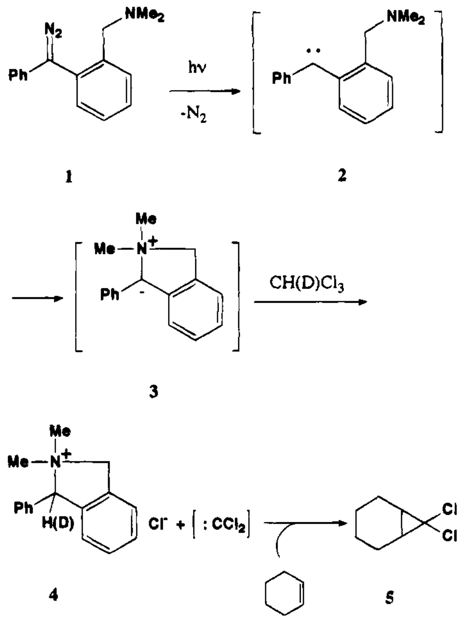
Scheme 2



The product was assigned as *N,N*-dimethyl-1-deuterio-1-phenylisoindolium chloride (**4**-*d*). The assignment was confirmed by the direct comparison of the spectrum of the product obtained in the irradiation of **1** in $CHCl_3$ with that of an authentic sample of **4**-*h*.

The formation of the isoindolium chloride is assumed to indicate that the carbene **2** undergoes intramolecular interaction with the dimethylamino nitrogen at the ortho position to generate ammonium ylide **3**,[8] which is then protonated to form the isoindolium trichloromethide as an initial product. Since it is well-known that $^-CCl_3$ anion easily undergoes elimination of Cl^- to give dichlorocarbene,[9] the trichloromethide salt must undergo similar degradation to afford the chloride salt **4**. This mechanistic scenario was easily confirmed by the observation that photolysis of **1** (4 mM) in $CHCl_3$ in the presence of cyclohexene (200 mM) produced dichloronorcarane (**5**, 26%) as a dichlorocarbene adduct. It may be that the carbene (**2**) undergoes insertion into the CH bond of $CHCl_3$ to produce (trichloromethyl)diphenylmethane which then undergoes intramolecular nucleophilic substitution by the amine to produce the trichloromethide salt. This possibility seems less probable since the CH bond of $CHCl_3$ is usually not very reactive toward carbenes, which, on the other hand, react with a chlorine atom of $CHCl_3$ more efficiently.[10] Moreover, a similar reaction, i.e., the attack of carbene on amine nitrogen to generate an ammonium ylide followed by protonation with chloroform to eventually produce the ammonium chloride and dichlorocarbene, is known in intermolecular reactions of halocarbenes with tertiary amines.[11]

More convincing evidence for the intervention of the ammonium ylide **3** was obtained by matrix isolation spectroscopic means. Thus, when the irradiation of **1** was carried out in a 2-methyltetrahydrofuran (2MTHF) matrix at 77 K, the matrix took on a deep purple color. In the UV–vis spectrum, the disappearance of the diazo spectrum and the formation of a broad intense band with a maximum near 540 nm, along with sharp, intense bands at 381 and 400 nm, were observed. The glassy solution did not exhibit any spectral change for several hours if kept at 77 K. However, warming it to room temperature and refreezing at 77 K led to the disappearance of all absorption bands (Figure 1). The optical absorption spectra of several diarylcarbenes in frozen media have been assigned. Typically they consist of an intense UV band and a weak visible transition.[12] These features are not present in the spectra obtianed from the photolysis of **1**. Several nitrogen ylides, on the other hand, have also been detected by laser flash photolysis techniques, and they usually show rather broad intense absorption bands in the visible region.[13] Moreover, similar irradiation of the trimethylammonium salt of **1** in a 2MTHF matrix did not result in the formation of the colored species but produced very weak visible absorption bands ascribable to the diarylcarbene. Under these circumstances, the purple-colored transient absorption is attributable to the ylide **3**.

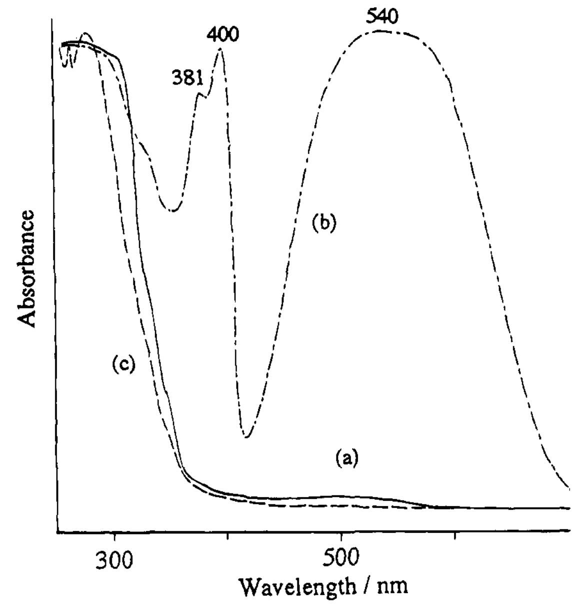


Figure 1. (a) (–) UV spectra of **1** in 2MTHF at 77 K. (b) (– • –) UV spectra obtained by irradiation of **1** in 2-MTHF at 77 K. (c) (– – –) Spectrum obtained after warming to room temperature.

Diphenylcarbene (**7**) generated from [2-[(*N,N*-dimethylamino)methyl]phenyl]phenyldiazomethane (**6**) gave somewhat different results (Scheme 3). Thus, irradiation of the diazomethane **6** in PhH proceeded cleanly in this case to afford two major products which were assigned as 3-phenyl-4-(*N,N*-dimethylamino)indan (**8**, 62%) and 2-[2-(*N,N*-dimethylamino)benzyl]styrene (**9**, 36%). The formation of **8** is explicable in terms of CH insertion of carbene **7**, while that of **9** must include a rearrangement,

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[8] A reviewer suggested that triazo intermediates presumably formed as a result of interaction of the excited diazo function with the amine nitrogen might be generated. However, the structure of the trapped product (i.e., **4**, **8**) and evolution of N_2 gas during the irradiation suggest that the ammonium ylides are the main intermediates.

[9] See, for example: Dehmlow, E. V.; Dehmlow, S. S. *Phase Transfer Catalysis*; Verlag Chemie: Weinheim, 1980.

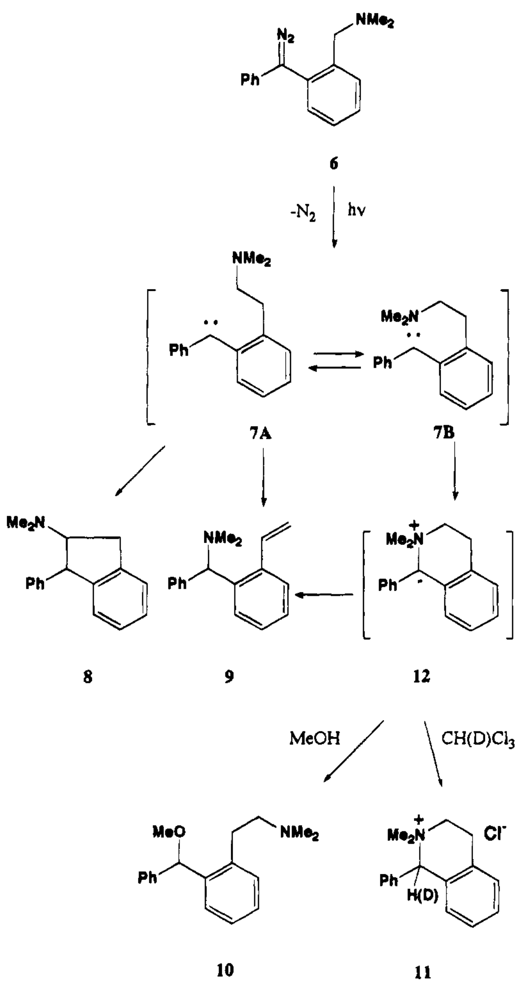
[10] Roth, H. D. *Acc. Chem. Res.* **1977**, *10*, 85.

[11] Dehmlow, E. V. Reference 1c, 1527 and references cited therein.

[12] See for reviews: (a) Trozzolo, A. M. *Acc. Chem. Res.* **1968**, *1*, 329. (b) Trozzolo, A. M.; Wasserman, E. In *Carbenes*; Moss, R. A., Jones, M., Jr., Eds.; Wiley: New York, 1973; Vol. 2, Chapter 5.

[13] For a reivew, see: Jackson, J. E.; Platz, M. S. In *Advances in Carbene Chemistry*; Brinker, U. H., Ed.; JAI Press: Greenwich, CT, 1994; Vol. 1, pp 89–160. Platz, M.; Maloney, V. M. In *Kinetics and Spectroscopy of Carbenes and Biradical*; Platz, M. S., Ed.; Plenum: New York, 1990; pp 239–352.

Scheme 3



presumably involving **7**. In order to get more insight into the reaction pathways leading to these products, the following control experiments were carried out. When the irradiation was carried out in PhH containing 1% MeOH, methyl ether **10** was produced in 11% yield at the expense of the styrene (23%), while the formation of indan **8** (59%) was not appreciably decreased. Similarly, photolysis of **6** in $CHCl_3$ also resulted in complete disappearance of the sytrene and concomitant formation of *N,N*-dimethyl-1-phenyldihydroquinolium chloride (**11**, 44%), the formation of **8** (40%) again being little affected. The results clearly suggest that the two products (**8** and **9**) were not formed from a common precursor. It is obvious that the quinolium chloride is produced from an ammonium ylide (**12**) that is formed as a result of intramolecular interaction of carbene with the amine, followed by protonation with $CHCl_3$. MeOH is then also expected to protonate the ylide to eventually lead to the ether. The styrene must be produced from the ylide by intramolecular Hofmann-type degradation since it is well-known that ammonium ylides that bear a β-hydrogen atom often undergo an elimination reaction to provide the corresponding amine and alkene.[6] Conceptually, the indan can also be produced from the ylide by Stevens rearrangement of a second, less stable ylide generated from the initial ylide **12**.[6] However, the trapping experiments clearly eliminated this possibility and suggested that the indan must be produced from carbene as a result of intramolecular C−H insertion.

A simple factor that controls the pathways leading to the ylide and C−H insertion is then the difference in the distance between the carbenic center and key reaction centers, i.e., amine nitrogen and β-CH bond. Thus, carbene has available two rotational isomers **7A** and **7B**, in terms of intramolecular reaction channels; in conformer **B** the carbenic center is easily trapped by the unshared electron pair on the amine nitrogen, while in **A** carbene interacts with the β-CH bonds. Product ratios might reflect, at least roughly, the relative population of each conformer. Predominant formation of the indane over the sytrene is not in accordance with the expectation that unshared electron pairs are usually more reactive than on electrons toward carbene and can be explained in terms of relative population of the conformers leading to the final products. Thus, conformer **B** is sterically less favorable than **A**. On the other hand, the β-CH bonds undergoing the insertion must be activated by the adjacent nitrogen.

It is important to examine the multiplicites responsible for the products. Kirmse and co-workers have proposed[14] in the intramolecular C−H insertion reaction of monophenylcarbene bearing 2-alkoxyalkyl substituents which lead to a five-membered ring product that, while the concerted insertion of the singlet involving the interaction of both p and σ orbitals of the carbene with the δ-C−H bonds is unfavored due to loss of benzylic stabilization and deformation caused by rotation of the bond connecting the divalent carbon to the benzene ring, abstraction of the δ-hydrogen to the half-filled, in-plane σ orbital of the triplet can proceed much more easily by way of a six-membered transition. Thus, it may be possible that **8** is produced by way of the triplet state of **7**, while the ylidic intermediate is obviously produced as a result of electrophilic attack of the singlet on the unshared electron pair of the amine nitrogen. In order to clarify this, photolysis of **6** in benzene was carried out in the presence of benzophenone as a triplet sensitizer. GC and ^{1}H NMR analysis of the photomixture indicated that neither **9** nor **8** was formed and that no prominant products were present in the mixture. This suggests that **6** is consumed mainly by single electron transfer from the amine to the excited benzophenone before it can be excited to the triplet excited state as a result of the energy transfer. The irradiation was then carried out in the presence of 1,4-cyclohexadiene, which is able to trap a triplet carbene by affording two hydrogens to produce the reduction products.[15] To our surprise, however, the formation of **9** was almost completely quenched in the presence of 5% of the diene while that of **8** was decreased very little, neither reduction product nor adducts with the diene being detected. The reason for this is not clear at present. A possible explanation might involve a quenching of the ylide by the diene, leading to **8**. It may be then that the ylide **12** is protonated to form 1-phenyldihydroquinolium, cyclohexadienyl anion, which then abstracts a proton from the 3-position of the quinolium to generate an ylide that leads to **8** by a Stevens rearrangement, and 1,3-cyclohexadiene. These control experiments failed to afford information about the multiplicites but again confirmed that **8** and **9** are produced from different intermediates.

Finally, the present carbenic route to the ylide was shown to have some notable regioselectivity. In order

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(14) Kirmse, W.; Özkir, I. S. *J. Am. Chem. Soc.* **1992**, *114*, 7590. Kirmse, W.; Ozkir, I. S.; Schnitzler, D. *J. Am. Chem. Soc.* **1993**, *115*, 792.

(15) See, for example: Tomioka, H.; Hirai, K.; Nakayama, T. *J. Am. Chem. Soc.* **1993**, *115*, 1285.

to verify the ylidic route to the sytrene, the 1-phenyl-1-deuterioquinolium chloride **11-*d*** obtained by the photolysis of **6** in $CDCl_3$ was treated with NaOEt. The aminostyrene was obtained quantitatively, as expected. However, ^1H NMR analysis showed that the styrene retained deuterium at the original position of the precursor salt. This indicates that the ylide produced in this experiment is an unstable methylene ylide obviously generated as a result of deprotonation of an ammonium methyl group, not the ylide obtained in the carbenic reaction. This is presumably due to steric restraints during the attack of the base on the salt.

The present observations show that the carbenic route to the ammonium ylide is feasible for those intramolecular systems in which formation of the desired ylides are somewhat sensitive to the structure of the precursor carbene. The ammonium ylides thus formed are detected not only by matrix isolation spectroscopy but also trapped by $CHCl_3$ to give the ammonium salts and dichlorocarbene.

Experimental Section

General Methods. GC−MS spectra were recorded with a GC column prepared from 5% silicone OV-17 on Diasolid L (5.0 mm × 1.0 m). ^1H and ^{13}C NMR spectra were recorded at 100 or 270 MHz. Column chromatography was carried out on a Fuji Davison silica gel BW-127ZH or ICN alumina (neutral). GLC was carried out on a column prepared from 5% silicone OV-17 on Diasolid L (5.0 mm × 2.0 m).

Low-Temperature Spectra at 77 K. Low-temperature UV/vis spectra at 77 K were obtianed by using a variable-temperature liquid nitrogen cryostat equipped with quartz outer windows and sapphire inner windows for irradiation and UV monitoring. The sample was dissolved in dry 2-methyltetrahydrofuran, placed in a long-necked quartz cuvette of 1-mm path length, and degassed by repeated freeze−degas−thaw cycles at pressure near 10^{-5} Torr. The cuvette placed in the cryostat was irradiated for several minutes in the spectrophotometer with a 500-W xenon arc lamp using a Pyrex filter, and the spectral changes were recorded at appropriate time intervals.

Materials. 2-[(*N,N*-Dimethylamino)methyl]benzophenone. A solution of 2-methylbenzophenone (4.0 g, 0.02 mol) in CCl_4 (40 mL) was heated under reflux and irradiated with a 300 W high-pressure Hg lamp while Br_2 (1.6 g 0.02 mol) in CCl_4 (5 mL) was added. Evaporation of the solvent gave an oil (5.3 g) whose ^1H NMR (CCl_4) showed signals at 4.62 ppm assignable to the side chain hydrogen atoms of 2-bromomethyl benzophenone, in addition to the methyl protons signals of the starting ketone appearing at δ 2.29. The reaction mixture whose ratios of the bromo ketone and the starting material determined by ^1H NMR spectra ranged from 6:4 to 8:2 was used to the next step without further purification since all attempts to isolate the bromo ketone resulted in the formation of 1-phenylisobenzofuran. Thus, to a solution of the brominated mixture containing a net 0.015 mol of the bromo ketone in anhydrous PhH (40 mL) was introduced Me_2NH (0.05 mol) at rt under vigorous stirring. The reaction mixture was extracted with 2 N HCl (20 mL × 7), and the extract was washed with PhH (30 mL × 3). The aqueous layer was made alkaline with $NaHCO_3$ and extracted with Et_2O (30 mL × 5). The ethereal phase was dried over Na_2SO_4 and evaporated to leave the [(dimethylamino)methyl]benzophenone as a yellowish liquid (2.8 g, 85%): ^1H NMR (CCl_4) 7.67 (dd, $J = 2.0$, 7.0 Hz, 2H), 7.49−7.09 (m, 7H), 3.40 (s, 2H), 1.90 (s, 6H).

[2-[(*N,N*-Dimethylamino)methyl]phenyl]phenyldiazomethane (1). A solution of [(dimethylamino)methyl]benzophenone (1.15 g, 4.81 mmol), hydrazine hydrate (4.68 mL, 96.2 mmol), and hydrazine hydrochloride (0.5 g, 4.81 mml) in anhydrous EtOH (30 mL) was placed in a 100 mL round bottom flask and was deaerated by repeated evacuation and purging with argon. This deaeration process was essential to obtain pure hydrazone in higher yield. The mixture was refluxed under argon until TLC monitoring showed that most of the ketone was consumed. After cooling, the solvent was evaporated and the mixture was added to Et_2O (30 mL). The ethereal solution was washed with H_2O (20 mL × 2), dried over Na_2SO_4 and evaporated to leave a semisolid, which was recrystalized from EtOH to give a reddish solid (1.17 g, 96%): mp 60−62 °C; ^1H NMR (CCl_4) δ 7.73−7.01 (m, 9H), 5.24 (bs, 2H), 3.31 (d, $J = 14.0$ Hz, 1H), 3.10 (d, $J = 14.0$ Hz, 1H), 2.69 (s, 6H).

The hydrazone (1.0 g, 3.9 mmol), anhydrous Et_2O (60 mL), anhydrous Na_2SO_4 (1.1 g), $Ba(MnO_4)_2$ (2.0 g, 5.3 mmol), and saturated ethanolic KOH (0.2 mL) were placed in a round-bottom flask, and the mixture was stirred in the dark for 20 h. After filtration, the solvent was removed on a rotary evaporator to afford the diazomethane (**1**) as a red liquid (1.0 g, 98%): ^1H NMR ($CDCl_3$) δ 7.68−6.80 (m, 9H), 3.40 (s, 2H), 2.19 (s, 6H); IR (KBr) 2050 cm^{-1}.

[2-[(*N,N*-Dimethylamino)ethyl]phenyl]phenyldiazomethane (6) was prepared by the procedure described above starting from *o*-(2-bromoethyl)benzophenone[16] [^1H NMR ($CDCl_3$) δ 7.81−7.72 (m, 2H), 7.61−7.23 (m, 7H), 3.58 (t, $J = 7.0$ Hz, 2H), 3.24 (t, $J = 7.0$ Hz, 2H)] by way of *o*-[2-(dimethylamino)ethyl]benzophenone [^1H NMR ($CDCl_3$) δ 7.89−7.80 (m, 2H), 7.62−7.25 (m, 2H), 2.92 (dd, $J = 6.0$, 9.0 Hz, 2H), 2.52 (dd, $J = 6.0$, 9.0 Hz, 2H), 2.10 (s, 6H)] and the corresponding hydrazone [^1H NMR ($CDCl_3$) δ 7.53−7.09 (m, 9H), 4.80−3.60 (bs, 2H), 2.69−2.56 (m, 2H), 2.49−2.29 (m, 2H)], 2.10 (s, 6H). Red oil: ^1H NMR ($CDCl_3$) δ 7.40−7.24 (m, 7H), 7.00−6.76 (m, 2H), 2.68 (m, 2H), 2.48 (m, 2H), 2.06 (s, 6H); IR (KBr) 2050 cm^{-1}.

Trimethylammonium iodide of 1 was prepared by stirring a solution of **1** (23 mg, 0.09 mmol) and MeI (1 g, 7 mmol) in anhydrous MeCN (1 mL) for 4 h, followed by addition of *n*-hexane and washing of the resulting precipitates with *n*-hexane to give a red solid (28 mg, 78%): ^1H NMR ($CDCl_3$) δ 8.09 (m, 1H), 7.72−7.08 (m, 7H), 7.00−6.81 (m, 1H), 4.79 (s, 2H), 3.36 (s, 9H); IR (KBr) 2050 cm^{-1}.

2-[2-(*N,N*-Dimethylamino)benzyl]styrene (9). To a solution of *o*-vinylbenzophenone (330 mg, 1.6 mmol) in absolute EtOH (10 mL) was added $NaBH_4$ (60 mg, 1.6 mmol) in one portion, and the resulting mixture was refluxed for 1 h. The solvent was evaporated, and the residue was added to Et_2O (30 mL) and H_2O (20 mL). The aqueous layer was washed with Et_2O (10 mL × 3), and the combined ethereal layer was washed with H_2O (20 mL × 2), dreid over Na_2SO_4, and evaporated to give *o*-vinylbenzhydrol as a yellowish viscous oil (314 mg, 94%): ^1H NMR ($CDCl_3$) δ 7.56−6.99 (m, 9H), 6.92 (dd, $J = 11.0$, 16.0 Hz, 1H), 6.05 (s, 1H), 5.58 (dd, $J = 1.0$, 16.0 Hz, 1H), 5.23 (dd, $J = 1.0$, 11.0 Hz, 1H), 2.05 (bs, 1H).

A solution of the benzhydrol (150 mg, 0.71 mmol) in anhydrous PhH (1.2 mL) was added to a stirred and cooled mixture of PBr_3 (0.05 mL, 0.57 mmol) and anhydrous pyridine (0.07 mL), and the mixture was stirred for 1 h. The mixture was added to H_2O (3 mL) and extracted with Et_2O (20 mL × 3). The ethereal layer was washed with H_2O (20 mL × 2), dried over Na_2SO_4, and evaporated to give 2-(bromobenzyl)styrene as a yellowish oil (184 mg, 96%): ^1H NMR ($CDCl_3$) δ 7.64−7.08 (m, 9H), 7.00 (dd, $J = 11.0$, 16.0 Hz, 1H), 6.57 (s, 1H), 5.63 (dd, $J = 1.0$, 16.0 Hz, 1H), 5.40 (dd, $J = 1.0$, 11.0 Hz, 1H).

To a solution of the bromide (200 mg, 0.66 mmol) in anhydrous PhH (1 mL) was introduced dry Me_2NH (2 mmol) through a KOH tube under vigorous stirring at rt. Usual workup of the mixture provided **9** as a yellow oil (82 mg, 53%): ^1H NMR ($CDCl_3$) δ 7.76 (dd, $J = 7.92$, 0.99 Hz, 1H), 7.42−7.11 (m, 9H), 5.50 (dd, $J = 17.33$, 1.65 Hz, 1H), 5.29 (dd, $J = 10.89$, 1.65 Hz, 1H), 4.41 (s, 1H), 2.18 (s, 6H); EIMS *m/e* (relative intensity) 237 (M^+, 42), 192 (65), 178 (63), 134 (60), 115 (100).

Isoindolium Chloride 4.[17] A solution of PhLi prepared

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[16] Fr. 1, 337, 060 (CI, C 07c), Sept 6, 1963; *Chem. Abstr.* **1964**, *60*, 2827d.

[17] Wittig, G.; Closs, G.; Mindermann, F. *Liebigs Ann. Chem.* **1955**, *594*, 89.

from PhBr (0.029 mol) and Li (0.029 mol) in anhydrous Et_2O (5 mL) was added dropwise into a stirred solution of *N*-methylphthalimide (0.029 mol) in anhydrous Et_2O (5 mL) under reflux. H_2O (30 mL) was added to the mixture which was extracted with $CHCl_3$ (20 mL × 3). Evaporation of the solvent gave crude product which was recrystallized from EtOAc to give 3-hydroxy-*N*-methylisoindolinone as a white solid (1.19 g, 17%): mp 182–185 °C; ^1H NMR ($CDCl_3$) δ 7.83–7.65 and 7.61–7.38 (m, 9H), 3.60 (bs, 1H), 2.79 (s, 3H).

A solution of the isoindolinone (200 mg, 0.84 mmol) in anhydrous THF (5 mL) was added to a stirred suspension of $LiAlH_4$ (100 mg, 2.6 mmol) in anhydrous THF (10 mL) at room temperature, and the mixture was refluxed for 1.5 h. Usual workup followed by TLC separation (Et_2O:petroleum ether = 3:7) afforded *N*-methyl-1-phenylisoindoline as a yellow oil (82 mg, 47%): ^1H NMR ($CDCl_3$) δ 7.38–7.10 (m, 9H), 6.77 (d, J = 7.25 Hz, 1H), 4.39 (d, J = 12.54 Hz, 1H), 3.77 (d, J = 12.54 Hz, 1H), 2.48 (s, 3H).

To a solution of the isoindoline (40 mg, 0.19 mmol) in anhydrous MeCN (0.7 mL) in a pressure bottle was introduced dry MeCl (1 mmol) at −78 °C, and the bottle was capped. After being stirred for 3 days at rt, the mixture was evaporated to dryness to leave **4** (31 mg, 63%): ^1H NMR ($CDCl_3$) δ 7.88–7.14 (m, 9H), 6.54 (s, 1H), 5.35 (d, J = 14.52 Hz, 1H), 5.16 (d, J = 14.52 Hz, 1H), 3.86 (s, 3H), 2.97 (s, 3H).

3-Phenyl-2-(dimethylamino)indan (8).[18] To a solution of $Me_2NH{\cdot}HCl$ (0.25 mmol) and KOH (20 mg) in MeOH (5 mL) was added 3-phenylindan-2-one (26 mg, 0.2 mmol) in one portion, and a solution of $NaBH_3CN$ (5 mg, 0.076 mmol) in MeOH (3 mL) was added to the stirred suspension. After the addition was complete, the suspension was stirred for 30 min and KOH (10 mg) was added. Usual workup gave **8** as yellow liquid (13 mg, 32%): ^1H NMR ($CDCl_3$) δ 7.33–7.14 (m, 9H), 6.76 (d, J = 7.25 Hz, 1H), 4.33 (d, J = 7.25 Hz, 1H), 3.47 (m, 1H), 3.21 (dd, J = 15.83, 7.59 Hz, 1H), 3.00 (dd, J = 15.83, 7.92 Hz, 1H), 2.26 (s, 6H); MS *m/e* (relative intensity) 237 (M^+, 100), 192 (65), 179 (51), 165 (50).

Irradiation for Product Identification. In a typical run, a solution of the diazomethane (ca. 30–50 mg) in anhydrous solvents (30 mL) was placed in a Pyrex tube, degassed by bubbling dry Ar, and irradiated with a high-pressure 300 W mercury lamp at 10 °C until all the diazo compound was destroyed. The irradiation mixture was then concentrated on a rotary evaporator below 20 °C. Individual components were isolated either by column chromatography or by preparative TLC and identified by NMR and MS.

Irradiation for Analytical Purposes. All irradiations were carried out in a Pyrex tube of 5.0 mL capacity. In order to avoid ambiguity in relative yields due to oxidation, the solution was degassed by subjecting the sample to a minimum of three freeze–degas–thaw cycles at pressure near 10^{-5} Torr before irradiation and the tube was sealed under reduced pressure. Irradiation was carried out with a filtered light from the mercury lamp through a Pyrex filter and generally continued until all the diazomethane was consumed. Product identifications were established either by GC–MS or by NMR comparison with authentic samples separated as above or prepared independently, and product distributions were conveniently determined by standard GC and NMR techniques.

Irradiation in MeOH. Irradidation was carried out as described above and the following methyl ethers were isolated almost quantitatively.

Phenyl[2-[(*N,N*-dimethylamino)methyl]phenyl]methly methyl ether: ^1H NMR ($CDCl_3$) δ 7.60–6.86 (m, 9H), 5.72 (s, 1H), 3.64–3.36 (m, 2H), 3.23 (s, 3H), 2.11 (s, 6H); MS *m/e* (relative intensity) 255 (M^+, 1.2), 240 (21), 179 (100).

Phenyl[2-[(*N,N*-dimethylamino)ethyl]phenyl]methyl methyl ether: ^1H NMR ($CDCl_3$) δ 7.64–7.09 (m, 9H), 5.52 (s, 1H), 3.46 (s, 3H), 2.97–2.73 (m, 2H), 2.47–2.39 (m, 2H), 2.21 (s, 6H); MS *m/e* (relative intensity) 269 (M^+, 2), 254 (25) 193 (100).

Irradiation of 1 in $CHCl_3$. Irradiation of **1** (30.0 mg) in anhydrous $CHCl_3$ (30 mL) gave the product whose ^1H NMR spectra were in complete agreement with that of the authentic isoindolium chloride (**4**). Irradiation of **1** in $CDCl_3$ in an NMR tube monitored by ^1H NMR showed that **4** was only detectable product.

Irradiation of 6. Photolysis of **6** in dry PhH, followed by preparative TLC, afforded the aminostyrene **9** and the aminoindan **8**, which were identified by comparison of their spectroscopic data with those of the authentic specimens.

Irradiation of **6** in anhydrous $CHCl_3$, followed by evaporation of the solvent and washing the residue with dry *n*-hexane gave the 1-phenylquinolium chloride (**11**, 52%) as a brownish solid: ^1H NMR ($CDCl_3$) δ 7.61–7.12 (m, 9H), 7.08 (d, J = 7.59 Hz, 2H), 4.18 (dt, J = 5.61, 5.94, 12.53 Hz, 2H), 3.90 (dt, J = 7.26, 7.59, 12.53 Hz, 2H), 3.69 (s, 3H), 3.25 (s, 3H). The aminostyrene (**9**) was recovered from the *n*-hexane washings. The identity of **11** was further established by the treating with NaOEt to give **9** quantitatively.

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Supplementary Material Available: Copies of ^1H NMR spectra of compounds **1**, **4**, **6**, **8**, **9**, **10**, and **11** (8 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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