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# Evidence for the Intermediacy of Pentaphenylethyl and Heptaphenylpropyl Cations in the Reaction of Triphenylmethyl Cation with Diphenyldiazomethane or Diphenylketene[1]

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**Abstract:** Electrophilic reactions of diphenyldiazomethane and diphenylketene with triphenylmethyl and nitrosonium cations as well as with iodine were investigated. Tetraphenylethylene was obtained in all cases. In the reaction of perdeuteriated triphenylmethyl cation with diphenyldiazomethane, phenyl scrambling gave evidence for the intermediate formation of pentaphenylethyl cation (**1**) (which undergoes facile 1,2-phenyl shift through the corresponding phenonium ion (**1a**)) and subsequently of the heptaphenylpropyl cation (**5**). Additional evidence for phenyl scrambling has also been obtained from $^{13}C$ labeling experiments. Diphenyldiazomethane and diphenyl- and di-*tert*-butylketenes were also protonated under superacidic conditions, and the resulting carbocations were characterized by $^{13}C$ NMR spectroscopy at low temperature.

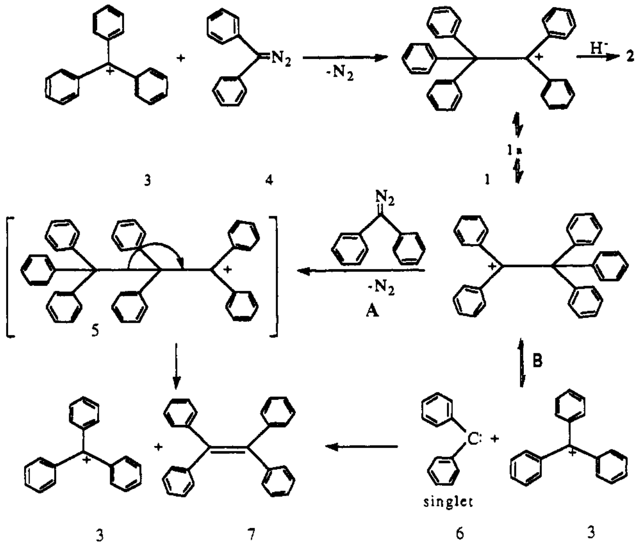
## Introduction

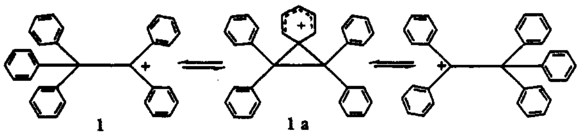
The pentaphenylethyl cation (**1**) is elusive, and its existence has never been directly proven.[2] The main difficulty appears to be the lack of availability of pentaphenylethyl derivatives. The only known pentaphenylethyl derivative is the parent hydrocarbon pentaphenylethane (**2**).[3] As a result of significant steric crowding no other derivative is known apart from ring tautomeric products. Consequently, only ionization of **2** could be attempted under superacidic stable ion conditions.[3] The attempts, however, led to the formation of triphenylmethyl cation and diphenylmethane.[2] An alternative approach to the pentaphenylethyl cation (**1**) is to investigate the reaction of triphenylmethyl cation with a diphenylcarbene precursor such as diphenyldiazomethane.

Diazo compounds are known to react with both electrophiles and nucleophiles. Such ambivalent character of diazo compounds has been illustrated in reactions with acids, metal salts, acid chlorides, carbonyl compounds, Grignard reagents, and diazonium salts.[4] Electrophilic reactions of diazomethane and aryl-substituted diazomethanes were reported by Whitlock[5,6] and others.[7,8] Of particular interest is the reaction of diphenyldiazomethane with triphenylmethyl cation giving tetraphenylethylene.[5,6] This reaction could involve the pentaphenylethyl cation (**1**) as an intermediate, but until now no evidence for it has been obtained. Alternatively, as shown by Creary[9] in the case of phenyldiazomethane, a single-electron-transfer pathway (SET) may be involved. However, under electrophilic reaction conditions the SET pathway appears unlikely.

In order to establish the intermediacy of **1** in the reaction of diphenyldiazomethane and triphenylmethyl cation and to probe for possible 1,2-phenyl migration in **1**, we have studied the reaction of both triphenylmethyl and perdeuteriated triphenylmethyl cations with diphenyldiazomethane in methylene chloride solution, giving tetraphenylethylene. If ion **1** were to be formed, it would be expected to undergo 1,2-phenyl migration through the intermediacy of the phenonium ion **1a**[10] and consequently phenyl group scrambling. The reaction was also carried out with $^{13}C$ enriched diphenyldiazomethane.

**Scheme I**





In addition to diphenyldiazomethane, reactions with isoelectronic diphenylketene and other related stable ketenes were also studied. Reactions of diphenyldiazomethane with other electrophiles such as $NO^+$ and $I_2$ were also carried out. Finally protonation studies of diphenyldiazomethane and disubstituted ketenes were also investigated under stable ion conditions, and the intermediate carbocations were characterized by $^{13}C$ NMR spectroscopy.

## Results and Discussion

Triphenylcarbenium tetrafluoroborate (Aldrich) in dry methylene chloride was treated with a solution of diphenyldiazomethane[11] in methylene chloride under a blanket of nitrogen at

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(1) Stable Carbocations. 281. For 280, see: Prakash, G. K. S.; Bausch, J. W.; Olah, A. G. *J. Am. Chem. Soc.* **1991**, *103*, 3203.

(2) Olah, G. A. et al., unpublished observations.

(3) Bachmann, W. E. *J. Am. Chem. Soc.* **1933**, *55*, 2135.

(4) Huisgen, R.; Fleischmann, R. *Justus Liebigs Ann. Chem.* **1959**, *47*, 623. More O'Ferrall, R. A. *Adv. Phys. Org. Chem.* **1967**, *5*, 331.

(5) Whitlock, H. W. *Tetrahedron Lett.* **1961**, 593.

(6) Whitlock, H. W. *J. Am. Chem. Soc.* **1962**, *84*, 2807.

(7) Bethell, D.; Handoo, K. L.; Farlhurst, S. A.; Sutcliffe, L. A. *J. Chem. Soc., Perkin Trans. 2* **1979**, 707.

(8) Bakke, J.; Bethell, D.; Parker, V. D. *Acta Chem. Scand.* **1987**, *41*, 253.

(9) Creary, X.; Wang, Y.-X.; Gill, W. *Tetrahedron Lett.* **1991**, *32*, 729.

(10) Lancelot, C. J.; Cram, D. J.; Schleyer, P. v. R. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley Interscience: New York, 1972; Vol. III, Chapter 27.

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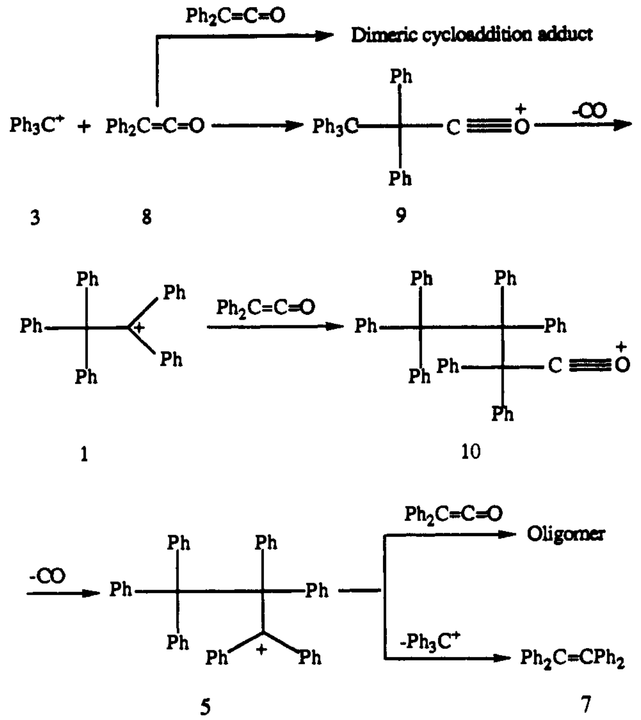
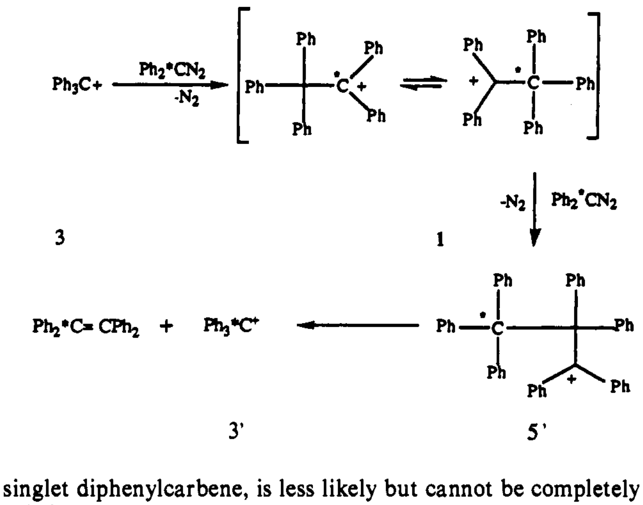
**Scheme II**



ambient temperature with rapid stirring.[12a] The deep red color of the diphenyldiazomethane gradually disappeared, and the mixture upon aqueous workup gave tetraphenylethylene in 79% isolated yield. A small amount (<0.2%) of pentaphenylethane (**2**) was also detected.[12b] The suggested mechanisms (A and B) for the triphenylmethyl cation-induced formation of tetraphenylethylene from diphenyldiazomethane are shown in Scheme I. Both mechanisms involve the formation of the pentaphenylethyl cation (**1**) as intermediate. Mechanism A additionally involves further formation of the heptaphenylpropyl cation (**5**). The observation of some pentaphenylethane (**2**) which must have been formed by hydride abstraction of the intermediate pentaphenylethyl cation from the solvent in competion with further reaction to tetraphenylethylene supports the intermediacy of ion **1**.

**Scheme III**



If highly crowded cation **1** were to undergo 1,2-phenyl shifts through the intermediacy of the phenonium ion **1a**, such rearrangement should lead to scrambling of the phenyl groups of the triphenylmethyl cation into the product tetraphenylethylene. To test this possibility we carried out the reaction with perdeuteriated triphenylmethyl cation, which should lead to deuterium labeled tetraphenylethylene.[13,14] The obtained tetraphenylethylene showed, besides unlabeled product, about 10% of labeled tetraphenylethylene incorporating two perdeuteriophenyl groups (by GC-MS analysis[15]), supporting the proposed mechanistic pathway A. Phenyl exchange in **1** via phenonium ion (**1a**), however, is clearly slow (90% of the product shows no phenyl scrambling). Ion **1** can then react further with diphenyldiazomethane, giving an even more crowded heptaphenylpropyl cation (**5**) which immediately cleaves to triphenylmethyl cation and tetraphenylethylene. Mechanistic pathway B, involving the formation of singlet diphenylcarbene, is less likely but cannot be completely ruled out.

Similarly, electrophilic reaction of diphenylketene[16] with trityl cation also gave tetraphenylethylene in 39% isolated yield. In this case the initial electrophilic attack results in the formation of the corresponding substituted acylium ion. The acylium ion then loses CO to generate intermediate **1**. On further reaction **1** reacts with diphenylketene followed by the loss of CO to give **5** which upon cleavage yields trityl cation and tetraphenylethylene, albeit in low yields. Presumably, the major competing side reactions are dimeric intermolecular cycloaddition of the labile diphenylketene as well as its oligomerization, which are depicted in Scheme II.

Efforts were also directed toward the generation and characterization of ion **1** under long-lived ion conditions. As mentioned previously, due to the lack of any pentaphenylethyl derivative, we could only attempt ionization of the parent pentaphenylethane under superacidic conditions which, however, resulted in C–C bond protolysis. For observing the pentaphenylethyl cation generated from the reaction of diphenyldiazomethane with triphenylmethyl cation, $^{13}$C-enriched diphenyldiazomethane was prepared and used for the reaction. The reaction was carried out in an NMR tube at −20 °C (initially the reactants were mixed at −78 °C) in deuterated methylene chloride solvent. The experiment was designed to generate the $^{13}$C-labeled carbocation center in **1** by the reaction of triphenylmethyl cation with $^{13}$C-enriched diphenyldiazomethane. If the intermediate pentaphenylethyl cation is produced and is stable at this temperature, the $^{13}$C-enriched carbocation center should be observable by $^{13}$C NMR even at very low concentrations. However, no stable, long-lived pentaphenylethyl cation was observed by NMR under these conditions. However, a $^{13}$C-enriched signal was observed at $\delta(^{13}C)$ 80 corresponding to the quaternary carbon of triphenylmethanol (obtained by hydrolysis). This again indicates 1,2-phenyl migration giving upon cleavage a $^{13}$C-labeled trityl cation, which when quenched with water gives the observed $^{13}$C-labeled triphenylmethanol (see Scheme III). This can be taken as additional evidence for phenyl scrambling in the pentaphenylethyl cation intermediate. Additional $^{13}$C-enriched absorptions for tetraphenylethylene were also observed, fully supporting the proposed mechanism of Scheme III.

The results obtained from the deuterium and $^{13}$C labeling experiments show that the pentaphenylethyl cation (**1**) is an intermediate in the reactions and that it undergoes 1,2-phenyl exchange (through the involvement of the phenonium cation **1a**).

Similar electrophilic reactions with nitrosonium tetrafluoroborate as well as with iodine were investigated. The obtained product in each case was again tetraphenylethylene. Iodine, an oxidizing agent, reacted with benzophenone hydrazone[17] directly

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(11) Barton, D. H. R.; O'Brien, R. E.; Sternhell, S. *J. Chem. Soc.* **1962**, 470. Smith, L. I.; Howard, K. L. *Organic Syntheses*; Wiley Interscience: New York, 1955; Collect. Vol. III, 351.

(12) (a) Reactions were carried out on a 10-mmol scale over a period of 75 min; (b) Mass spectra fragmentation was authenticated using a sample of pentaphenylethane independently prepared.[3]

(13) Dauben, H. J., Jr.; Honnen, L. R.; Harman, K. M. *J. Org. Chem.* **1960**, *25*, 1442.

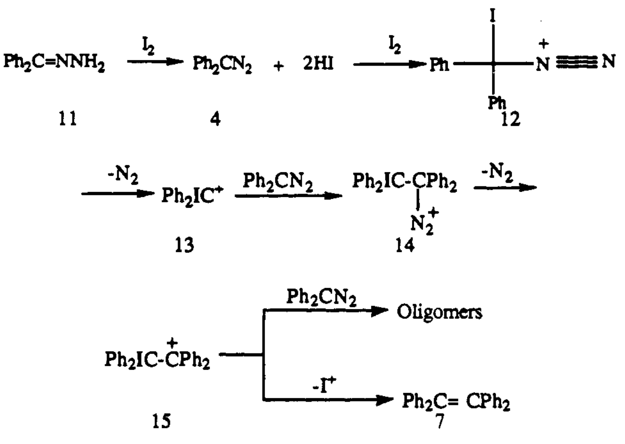
(14) Vogel, A. I. *A Text Book of Practical Organic Chemistry*, 3rd ed.; Longman Group: London, 1972; p 535.

(15) GC-MS analysis was performed on a Finnigan Incos-50 spectrometer equipped with DB-5 silica-quartz column.

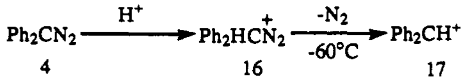
(16) Smith, L. I.; Hoehn, H. H. *Organic Syntheses*; Wiley Interscience: New York, 1955; Collect. Vol. III, 356.

(17) Barton, D. H. R.; Bashiardes, G.; Fourrey, J. *Tetrahedron* **1988**, *44(1)*, 147.

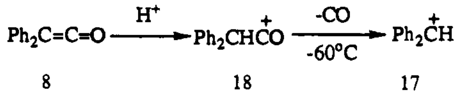
Scheme IV



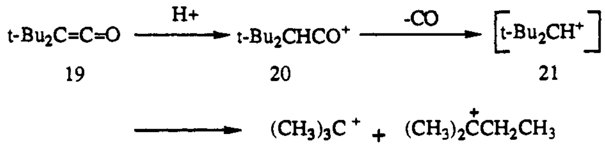
Scheme V



Scheme VI



Scheme VII



to give diphenyldiazomethane, and further reaction with electrophilic iodine led to the formation of tetraphenylethylene. Direct treatment of diphenyldiazomethane with $I_2$ also led to tetraphenylethylene. The proposed mechanism for the reaction is also similar to that of the reaction of trityl cation with diphenyldiazomethane. As depicted in Scheme IV, intermediate diphenyliodocarbenium ion (**13**) is involved during the course of the reaction.

The protonation of diphenyldiazomethane in Magic Acid ($FSO_3H/SbF_5$)/$SO_2ClF$ was also investigated using low temperature $^{13}C$ NMR and showed exclusive formation of benzhydryl cation (**17**) ($\delta(^{13}C)$ $C^+$, 200.6),[18a] as shown in Scheme V. The protonation of the parent diazomethane has been investigated previously.[18b] Protonation of diphenylketene and di-*tert*-butylketene[19] in Magic Acid solution at −60 °C resulted in the formation of diphenylaetylium ion (**18**) ($\delta(^{13}C)$ $CO^+$, 154.7) and di-*tert*-butylacetylium ion (**20**) ($\delta(^{13}C)$ $CO^+$, 155.3), respectively. The obtained $^{13}C$ NMR data are consistent with those of substituted acylium cations reported in the literature.[20] Decarbonylation of the acylium cations occurs readily upon warming to give their respective cations as shown in Schemes VI and VII. The di-*tert*-butylmethyl cation (**21**) further decomposes to give a mixture of *tert*-butyl cation (**22**) and *tert*-amyl cation (**23**).[21]

These observations clearly show that in these systems protonation exclusively occurs at $\alpha$-carbon followed by the loss of CO or $N_2$, as in the case of the trityl cation.

Evidence was also obtained via control experiments showing that for both diphenyldiazomethane and diphenylketene under the same reaction conditions and in the absence of electrophilic initiators, no tetraphenylethylene was obtained even after prolonged reaction time (ca. 4 h). This strongly suggests the need for electrophiles to initiate the reactions to give tetraphenylethylene as the final product.

From these observations one can expect the role of electrophiles including trityl cation to be similar. The scrambling experiment strongly supports the proposed mechanism in Scheme I through the formation of the carbocationic intermediates **1** and **5** when the electrophile is the trityl cation.

## Conclusion

In summary, the results obtained from the deuterium and $^{13}C$ labeling experiments show that the pentaphenylethyl cation (**1**) is an intermediate in the reaction of the trityl cation with diphenyldiazomethane or diphenyl ketene. Ion **1** undergoes 1,2-phenyl exchange through the involvement of the phenonium cation **1a**. Similar results favoring the proposed mechanism in Scheme I were also obtained from the respective electrophilic reactions of nitrosonium ion or iodine with diphenyldiazomethane. Low temperature $^{13}C$ NMR studies of the protonation of diphenyldiazomethane and disubstituted ketenes give only derived dediazonated or decarbonylated carbenium ions under stable ion conditions.

We are continuing our efforts directed toward obtaining and characterizing ion **1** under long-lived stable ion conditions by other approaches.

## Experimental Section

Triphenylmethyl (trityl) tetrafluoroborate, nitrosonium tetrafluoroborate, and iodine were commercially available and used as such. Perdeuteriated triphenylmethyl tetrafluoroborate, diphenylketene,[16] di-*tert*-butylketene,[19] diphenyldiazomethane, and $^{13}C$ labeled diphenyldiazomethane[11] were prepared according to literature procedures. The soninications were carried out in an American Scientific Products Laboratory Sonicator. Gas chromatographic analysis was carried out on a Varian (Model 3700) gas chromatograph using a silica–quartz capillary column coated with DB-1. Mass spectroscopic analysis was performed on a Finnigan INCOS-50 GC-MS spectrometer. NMR spectra were recorded on a Varian-200 MHz (VXR-200) superconducting NMR spectrometer equipped with a broad-band variable temperature probe. All $^{13}C$ chemical shifts are referenced from external capillary tetramethylsilane or deuteriochloroform signal.

**Preparation of Deuterium-Labeled Trityl Tetrafluoroborate.** Dried hexadeuteriobenzene was brominated using a literature procedure.[14] The Grignard reagent from the resulting bromobenzene was reacted with diethyl carbonate ($^1/_3$ equiv) to give the corresponding trityl carbinol after a water quench. Perdeuteriotrityl carbinol was reacted with tetrafluoroboric acid (48%) using a literature procedure to give the corresponding perdeuteriotrityl tetrafluoroborate.

**Reaction of Trityl Cation with Diphenyldiazomethane.** To a stirred solution of trityl tetrafluoroborate (10 mmol) in dry methylene chloride was dropwise added over a period of 15 min a solution of diphenyldiazomethane (5 mmol) in dry methylene chloride (10 mL). After the addition of the diazomethane was completed, the reaction mixture was stirred for 1 h. The mixture was then diluted with diethyl ether and quenched with water. After extraction with diethyl ether (3 × 50 mL), the combined organic layers were dried over anhydrous magnesium sulfate, filtered, and evaporated in vacuum to give a crude product which was further purified via column chromatography on silica gel (hexane eluent) to give tetraphenylethylene (0.66 g, 79% yield). A similar reaction was carried out with deuterium-labeled trityl tetrafluoroborate (1 mmol-scale). The obtained tetraphenylethylene product indicated roughly 10% deuterium incorporation by comparing *m/e* 332 vs 342 peaks.

**Reaction of Trityl Cation with Diphenylketene.** To a stirred solution of trityl tetrafluoroborate (10 mmol) in dry methylene chloride (10 mL) was dropwise added a solution of diphenylketene (5 mmol) in dry methylene chloride (10 mL) under a nitrogen atmosphere over a period of 15 min. After the addition of the ketene was completed the reaction mixture was stirred for another 1 h. The reaction mixture was diluted with diethyl ether and quenched with water. Extraction was carried out

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(18) (a) Olah, G. A.; White, A. M. *J. Am. Chem. Soc.* **1969**, *91*, 5801. (b) McGarrity, J. F.; Cox, D. P. *J. Am. Chem. Soc.* **1983**, *105*, 3961.

(19) Newman, M. S.; Arkell, A.; Fukunaga, T. *J. Am. Chem. Soc.* **1960**, *82*, 2498.

(20) Olah, G. A.; Kuhn, S. J.; Beke, S. *Chem. Ber.* **1956**, *89*, 862. Olah, G. A.; Kuhn, S. J.; Tolgyesi, W. S.; Baker, E. B. *J. Am. Chem. Soc.* **1962**, *84*, 2733. Tolgyesi, W. S.; Kuhn, S. J.; Moffat, M. E.; Bastien, I. J.; Baker, E. B. *J. Am. Chem. Soc.* **1963**, *85*, 1328.

(21) Olah, G. A.; Wu, A.; Farooq, O.; Prakash, G. K. S. *J. Org. Chem.* **1990**, *55*, 1792.

(22) Mackenzie, E. *J. Chem. Soc.* **1922**, *121*, 1697.

with methylene chloride (3 × 50 mL), and the combined organic layers were dried over anhydrous magnesium sulfate, filtered, and evaporated in vacuum to give a crude product which was further purified by column chromatography on silica gel to give tetraphenylethylene (0.32 g, 39% yield).

**Preparation of $^{13}$C-Labeled Diphenyldiazomethane.** $^{13}$C-Labeled benzoic acid (Aldrich) was reacted with phosphorus pentachloride using a literature procedure.[14] The resulting benzoyl chloride was refluxed in dried benzene in the presence of aluminum trichloride to give $^{13}$C-labeled benzophenone. The corresponding benzophenone hydrazone and diphenyldiazomethane were then obtained using a literature procedure.[11]

**Reaction of Trityl Cation with $^{13}$C-Labeled Diphenyldiazomethane.** A 5-mm NMR tube was charged with trityl tetrafluoroborate (20 mg), and deuteriated methylene chloride (1 mL) was added. The spectrum of the trityl cation was taken at −20 °C. $^{13}$C-Labeled diphenyldiazomethane (30 mg) was then added into the NMR tube at −78 °C. The NMR tube was briefly shaken to complete the reaction, and the reaction mixture was immediately analyzed by $^{13}$C NMR spectroscopy at −20 °C.

**Reaction of Nitrosonium Tetrafluoroborate with Diphenyldiazomethane.** To an ultrasound-agitated suspension of nitrosonium tetrafluoroborate (10 mmol) in dry 1,1,2-trifluorotrichloroethane (Freon-113) (10 mL) was added dropwise a solution of diphenyldiazomethane (5 mmol) in dry Freon-113 (10 mL) over a period of 15 min. After addition, the reaction mixture was sonicated further for an hour. Subsequently the reaction mixture was quenched with water. Extraction was carried out with dichloromethane (3 × 50 mL), and the combined organic layers were dried over anhydrous magnesium sulfate, filtered, and evaporated in vacuum to leave a crude material which was purified via column chromatography on silica gel (hexane eluent) to afford tetraphenylethylene (0.58 g, 70% yield). Sonication was necessary for the reaction to occur.

**Reaction of Iodine with Diphenyldiazomethane.** A mixture of iodine (10 mmol) and benzophenone hydrazone (5 mmol) was suspended in 10 mL of dry 1,1,2-trifluorotrichloroethane (Freon-113) and agitated with ultrasound for 3 h. The reaction mixture was then quenched with water. After being extracted with dichloromethane (3 × 50 mL), the combined organic layers were dried over anhydrous magnesium sulfate, filtered, and evaporated in vacuum to leave a crude product which was further purified via column chromatography on silica gel to give tetraphenylethylene (0.42 g, 51% yield).

**Reaction of Nitrosonium Tetrafluoroborate with Diphenylketene.** To an ultrasound-agitated suspension of nitrosonium tetrafluoroborate (5 mmol) in 10 mL of dry 1,1,2-trifluorotrichloroethane (Freon-113) was dropwise added a solution of diphenylketene (10 mmol) in dry Freon-113 (10 mL) over a period of 15 min. After completion of the addition of ketene, the reaction mixture was further sonicated for 1 h and was then quenched with water. After being extracted with dichloromethane (3 × 50 mL), the combined organic layers were dried over anhydrous magnesium sulfate, filtered, and evaporated in vacuum to leave a crude product which was purified via column chromatography on silica gel to give tetraphenylethylene (0.22 g, 27% yield).

**Reaction of Iodine with Diphenylketene.** Iodine (5 mmol) and diphenylketene (5 mmol) were treated in Freon-113 solvent (10 mL) as above, and the reaction mixture after workup and purification gave tetraphenylethylene (0.15 g, 18% yield).

**Protonation of Diphenyldiazomethane.** To a 5-mm NMR tube charged with diphenyldiazomethane (20.0 mg, 0.1 mmol) and freshly distilled $SO_2ClF$ (1.0 mL) was added fluorosulfonic acid/antimony pentafluoride (0.2 mL) at −60 °C (in a dry ice/acetone external cold bath). After vigorous stirring, a homogeneous solution was obtained. The $^{13}$C NMR spectrum was obtained at −60 °C and gave absorptions at $\delta(^{13}C)$ 200.6, 142.2, 129.5, 128.7, and 127.5.

**Protonation of Diphenylketene.** To a 5-mm NMR tube charged with diphenylketene (20.0 mg, 0.1 mmol) and freshly distilled $SO_2ClF$ (1.0 mL) was added fluorosulfonic acid/antimony pentafluoride (0.2 mL) and maintained at −60 °C (using a dry ice/acetone external cold bath). After vigorous shaking, a clear solution was obtained. $^{13}$C NMR spectroscopy at −60 °C showed absorptions at $\delta(^{13}C)$ 154.7, 139.8, 129.5, 128.7, 127.8, and 48.9, which correspond to diphenylacetylium ion.

**Protonation of Di-*tert*-butylketene.** To a 5-mm NMR tube charged with di-*tert*-butylketene (20.0 mg; 0.1 mmol) and freshly distilled $SO_2ClF$ (1.0 mL) was added fluorosulfonic acid/antimony pentafluoride (0.2 mL) at −60 °C. After vigorous shaking, a homogeneous solution was obtained. $^{13}$C NMR at −60 °C showed absorptions at $\delta(^{13}C)$ 154.1, 49.8, 41.3, and 26.6, corresponding to the di-*tert*-butyl acetylium ion. Upon warming the solution, rearrangement occurred with a loss of CO to give a mixture of *tert*-butyl and *tert*-amyl cations (**22** and **23**).

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# Photochemistry of (2-Nitrophenyl)diazomethane Studied by the Matrix Isolation Technique. (Nitrophenyl)carbene to (Carboxylphenyl)nitrene Rearrangement by Successive Reduction of the Nitro Group with the Carbenic Center

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**Abstract:** Irradiation (λ > 350 nm) of (2-nitrophenyl)diazomethane (**1**) matrix-isolated in Ar at 10 K provided 2-nitrosobenzaldehyde (**3**) presumably as a result of intramolecular oxygen migration in (2-nitrophenyl)carbene (**2**). Upon further irradiation (λ < 350 nm), **3** was decomposed to give a mixture of 2,1-benzisoxazol-3(1*H*)-one (**4**) and carbonylcyclopentadiene imine (**5**) along with $CO_2$. The oxazolone (**4**) underwent decarboxylation to give **5** upon irradiation with shorter wavelength light (λ > 300 nm) but not at longer wavelength (λ > 350 nm), suggesting **4** is not the direct precursor for **5** in the photolysis of **3**. Irradiation (λ > 350 nm) of (4-*n*-butyl-2-nitrophenyl)diazomethane (**1b**) under similar conditions resulted in the formation of carbonyloximinocyclohexadienylidene (**7**) which then produced the oxazolone (**4b**) and the imine (**5b**) upon further irradiation, suggesting that a 1,4-biradical generated as a result of abstraction of H at the ortho position by the photoexcited nitroso group was involved in the reaction of **3** forming **4**. (2-Carboxyphenyl)nitrene (**9**) generated by 1,4-OH shift in the 1,4-biradical was postulated as an intermediate leading to **5**, and this was actually demonstrated by independent generation of **9** by the photolysis of 2-azidobenzoic acid (**8**).

Since the pioneering work by Chapman and his co-workers,[1] matrix isolation techniques have shown their greatest power for investigating carbene chemistry.[2] These techniques not only enable us to observe and characterize these highly reactive species

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