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REACTION OF TRIFLIC ANHYDRIDE WITH DIAZOCOMPOUNDS

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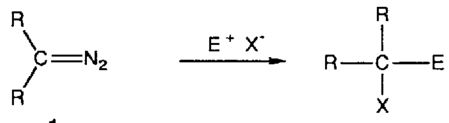
Summary Triflic anhydride reacts with aryldiazomethanes to form predominantly *cis*-stilbenes by a mechanism initiated by electron transfer from the diazocompounds to the anhydride

Diazocompounds are readily protonated under acidic conditions[1] They also undergo facile reaction with electrophiles such as halogen,[2] t-BuOCl,[3] and PhSCl[4] These reactions proceed by interaction of the electrophile with the nucleophilic carbon atom of the diazocompound, followed by loss of molecular nitrogen and bonding with available nucleophile α-Diazoketones react with the electrophilic reagent triflic anhydride, $(CF_3SO_2)_2O$, to give bis-enol triflates by a mechanism involving sulfonation at oxygen of the nucleophilic carbonyl group[5]



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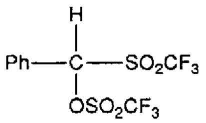

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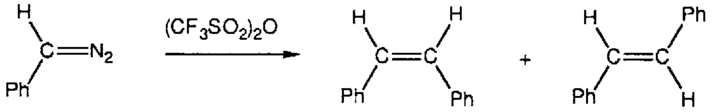
Interest in such reactions of diazocompounds with electrophiles has prompted us to react phenyldiazomethane, **4**, with triflic anhydride It was initially anticipated that such a reaction would lead to formation of the α-sulfonyl triflate **3** which would be derived from triflic anhydride acting in an electrophilic manner with the nucleophilic carbon of phenyldiazomethane When phenyldiazomethane is reacted with triflic anhydride (1 equivalent) at -78 °C to -50 °C in methylene chloride, the phenyldiazomethane is completely consumed However none of the expected product **3** was detected Instead *cis* and *trans*-stilbenes were isolated in a 93 7 ratio (90% overall yield) The reaction is catalytic in triflic anhydride Decreasing the amount of triflic anhydride to 15% also induces formation of stilbenes, but as expected, reaction does not occur at a convenient rate until about -40 °C A variety of aryldiazomethanes also undergo this reaction[6] Qualitatively, the reactivity order is $p\text{-}CH_3C_6H_4CHN_2 > C_6H_5CHN_2 > p\text{-}CF_3C_6H_4CHN_2$ Electron withdrawing groups therefore retard reaction rate Diphenyldiazomethane also gives an analogous dimeric product, tetraphenylethylene, along with some benzophenone azine



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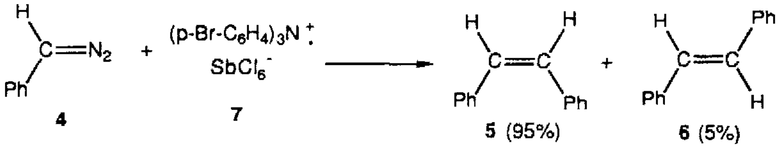
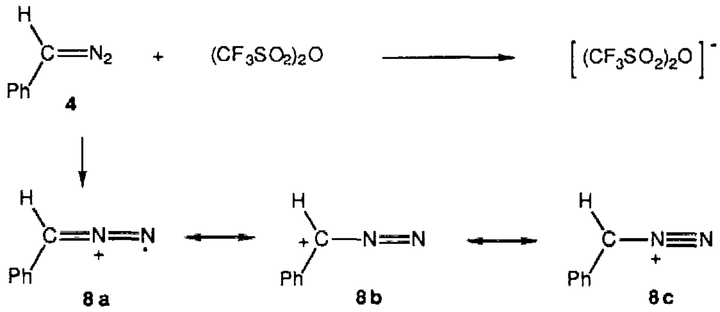
5 (93%)

6 (7%)

Concerning reaction mechanism, a process involving nucleophilic attack of the diazocompound on triflic anhydride does not lead to intermediates that can subsequently be transformed to stilbene by an obvious route We have therefore considered the possibility that triflic anhydride could initiate the formation of stilbenes from aryldiazomethanes by a single electron transfer process Phenyldiazomethane has therefore been reacted with the radical cation aminium salt **7** [7] At -78 °C, 1 mole % of **7** leads to rapid formation of stilbenes (90% yield, 95 5 ratio)



The similarity of the product ratios in the reaction of phenyldiazomethane with the triflic anhydride and with the radical cation salt **7** supports the suggestion that triflic anhydride can indeed initiate reactions of diazocompounds by electron transfer processes Also in support of this suggestion is the previous report that cerium (IV) salts can also promote formation of predominantly *cis*-stilbene from phenyldiazomethane [8] It was suggested that the phenyldiazomethane radical cation, **8**, formed by oxidation with Ce(IV), initiates these reactions Triflic anhydride and the radical cation salt **7** should also be able to promote formation of the phenyldiazomethane radical cation, **8**

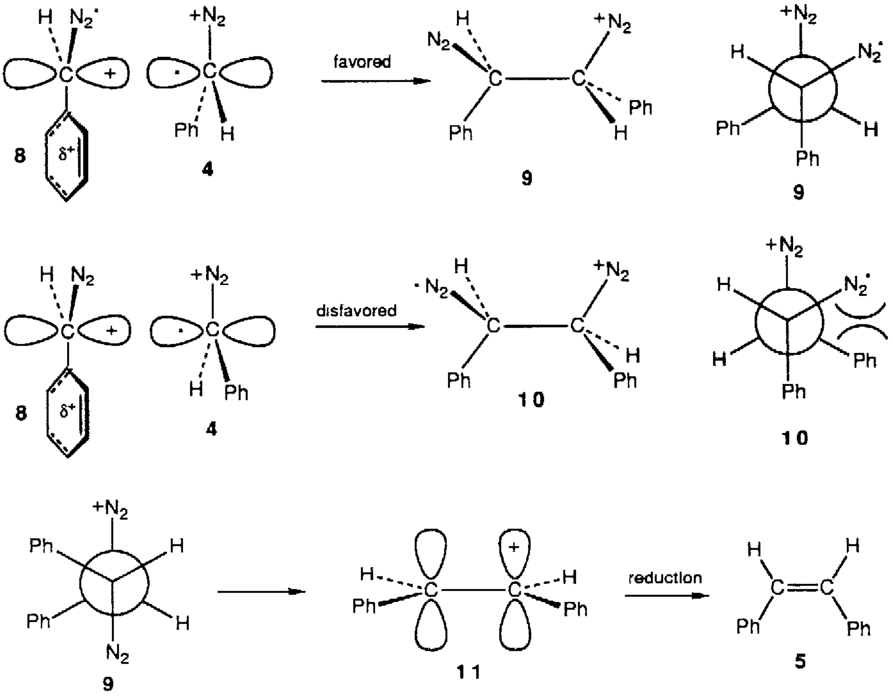


*Diphenyldiazomethane has been previously reacted with the radical cation salt **7**, and tetraphenylethylene was* produced, along with benzophenone azine [9] The reaction was initially proposed to involve coupling of the diphenyldiazomethane radical cation with unreacted diphenyldiazomethane and loss of nitrogen However subsequent studies[10] led to proposal of an acid catalyzed process The source of acid was reaction of the radical cation intermediate with a trace of some nucleophile Reaction of diphenyldiazomethane with acid led to the benzhydryl cation and coupling with unreacted diphenyldiazomethane led to tetraphenylethylene *This acid catalyzed mechanism is considered unlikely in the reaction of phenyldiazomethane, **4**, with triflic anhydride or the aminium salt **7*** for the following reasons Reaction of phenyldiazomethane, **4**, with 5 mole % CF_3SO_3H (which is more acid than could be produced from **7** or triflic anhydride under our reaction conditions), requires several hours at room temperature to complete the reaction of **4** By way of contrast, 1 mole % of **7** leads to complete disappearance of **4** at -78 °C, and 15 mole % of triflic anhydride leads to complete reaction of **4** at -40 °C Therefore the reactions of phenyldiazomethane with triflic anhydride or **7** are far too rapid to be acid catalyzed Secondly, reaction of phenyldiazomethane, **4**, with CF_3SO_3H, gave a low yield (34%) of *cis* and *trans*-stilbenes (51 49 cis/trans ratio)

Therefore the triflic acid catalyzed reaction of phenyldiazomethane gave a substantially different product ratio in a significantly lower yield at a much slower rate than the triflic anhydride and the aminium salt catalyzed reactions

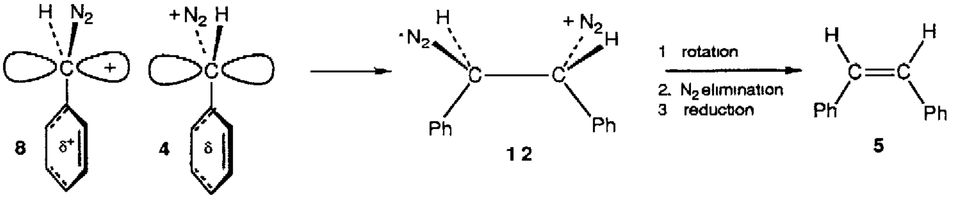
While a mechanism initiated by electron transfer to triflic anhydride appears likely, no explanation has been offered for the predominant formation of *cis*-stilbene from the phenyldiazomethane radical cation, **8** In a related process, aryldiazomethanes have been found to react with rhodium (II) catalysts to form predominantly *cis*-stilbene [11] A mechanism involving coupling of a rhodium complexed carbene with diazocompound has been suggested [11] The stereochemical outcome was rationalized by an attractive interaction between the diazonium group and the rhodium in the coupling process A steric factor led to preferred formation of one complex, and subsequent trans elimination of rhodium and nitrogen gave predominantly *cis*-stilbene Obviously, this rationale offered for rhodium catalyzed reaction[11] cannot be operative in the triflic anhydride promoted reaction since there is no metal present

We suggest that steric and electrostatic interactions can also account for the formation of *cis*-stilbene when the radical cation **8** couples with phenyldiazomethane, **4** In the radical cation **8**, positive charge is undoubtedly delocalized onto the aromatic ring as suggested by form **8b** An unfavorable electrostatic interaction between the electron deficient ring of **8** and the developing diazonium functionality causes approach of **8a** to **4** to occur as shown in **9** (Ph and N_2^+ anti) Of the two possible approaches, the one leading to **9** is favored over the approach leading to **10** for the steric reasons illustrated in the Newman projection of **10** If loss of molecular nitrogen from **9** occurs when



the nitrogens are in an anti conformation, then the cis radical cation **11** would result While radical cations such as **11** are known to undergo facile isomerization,[12] it is suggested that, at the low temperatures used in our studies, reduction of **11** occurs before rotation Hence *cis*-stilbenes are the major product

An alternative, and potentially cooperative interaction that would also lead to *cis*-stilbene, is shown below We have used NMR methods[13] to determine σ_I (0 13) and σ_R (-0 23) values for the CHN_2 group The CHN_2 group is therefore a net electron donor group An attractive interaction between the electron deficient aromatic ring of **8** and an electron rich ring of **4** would yield **12**, and subsequently, *cis*-stilbene



In conclusion, these studies illustrate the oxidative properties of triflic anhydride,[14] which can promote the formation of *cis*-stilbenes from aryldiazomethanes by a single electron transfer initiated process

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(6) In a typical procedure, a solution of 159 mg of triflic anhydride in 3 mL of CH_2Cl_2 was added dropwise to a solution of 445 mg of **4** in 5 mL of CH_2Cl_2 at -78 °C The mixture was warmed to -40 °C until the red color disappeared (2 hr) An aqueous solution of Na_2CO_3 was added and a standard aqueous workup followed Chromatography on a short silica gel column and elution with hexanes gave 273 mg of **5** and **6** in a 93 7 ratio

(7) This salt has been found to catalyze cyclopropanation of alkenes by ethyl diazoacetate by a mechanism involving the alkene radical cation See Bauld N Stufflebeme, G W , Lorenz, K T *J Phys Org Chem* **1989**, 2, 585

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(14) For a previous study illustrating the oxidative properties of $(CF_3SO_2)_2O$ see Creary, X *J Org Chem* **1980**, 45, 2727

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