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Engineering Reactions in Crystalline Solids: Prediction of Intramolecular Carbene Rearrangements

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Abstract—The unimolecular reactivity and stereoselectivity of four arylalkyl carbenes generated by a steady state irradiation of crystalline 1,2-diaryldiazopropanes were correctly predicted by taking advantage of known reaction trajectories applied to structures obtained by simple molecular mechanics calculations. It is suggested that the conformation of the diazo compound in the crystal determines the conformation of the carbene intermediate which is predisposed for a conformationally stereospecific 1,2-H shift. The results of irradiations of 1,2-diaryldiazoalkanes in crystalline media were compared with those obtained in solution and in amorphous solids. It was demonstrated that rigidity alone is not sufficient for carbene reactions to proceed with high stereoselectivity. © 2000 Published by Elsevier Science Ltd.

Introduction

Although reactions in crystals are severely limited by structural and energetic constraints, they have been shown to deliver some of the most impressive chemical demonstrations and mechanistic detail.[1–6] With examples that include numerous cases of efficient asymmetric synthesis,[7,8] the generation of single crystalline polymers,[9] and selective reactions without solvents,[10,11] the potential of crystal chemistry is enormous. An immediate challenge in the field of crystal chemistry is the need of strategies to design solid state reactions in a reliable manner to establish the rules that will allow us to exploit their potential and avoid their shortcomings. To accomplish this, the topochemical postulate provides structural guidelines by stating that reactions in crystals can only occur with a minimum of atomic and molecular motion.[1,12,13] However, it is difficult to design viable chemical reactions in solids based only on structural constraints when there is no knowledge of reaction energetics. For that reason, during the last few years we have explored an energetic viewpoint of the topochemical postulate: *reactions in crystals must occur under conditions where translational and rotational kinetic energy are kept to a minimum*. A logical mechanistic implication of this viewpoint would be that reactions in crystals will be more favorable with reagents that have a very high energy content, and with reactions that occur by quantum mechanical tunneling from their lower vibrational states.[14–16] Chemical species rich in potential energy will have a wide variety of highly exothermic reactions by breaking weak bonds and making strong ones despite severe structural constraints. At the same time, species with high potential energy will have early transition states and relatively low activation barriers, as suggested by the Hammond postulate.

With energetic guidelines in mind, and with the purpose of engineering reactions in crystals in a reliable manner, we have taken advantage of stable compounds that are capable of generating chemical species with high energy content. We have analyzed crystals of stable compounds that can generate carbenes,[6,17–19] nitrenes,[20] biradicals,[5,21,22] and radical pairs.[23] Crystalline diazo compounds, in particular, generate highly reactive carbenes that can undergo a wide variety of exothermic processes with low activation energies.[24,25] Since their rates of reaction tend to be near diffusion and conformational control, the rate-limiting and selectivity-determining steps are strongly influenced by environmental factors such as viscosity and polarity.[24,26–28] We have recently shown that photochemical irradiation of crystals of biphenyl-substituted diazopropane **1a** results in the nearly exclusive formation of the alkene **(Z)-3a** by a highly selective 1,2-H shift of the arylalkylcarbene intermediate **2a** (Scheme 1).[6,17,19]

Irradiation of **1a** in a variety of solvents led to **(Z)-3a**, **(*E*)-3a**, **(*Z*)-4a**, and **(*E*)-4a**, in addition to (**5**) from solvent insertion in EtOH and azines by reaction between carbene and diazo compounds at high diazo concentration. Differences in stereoselectivity in solution and in the solid state were rationalized by recognizing that crystals prevent bimolecular reactions between carbenes and diazo molecules and that different conformers give rise to different products (Fig. 1). As suggested by the horizontal arrows in Fig. 1, chemical reactions in solution explore a wide variety of rapidly equilibrating conformational isomers and bimolecular collisions (not shown), while reactions in crystals are generally restricted to one conformational isomer. It was

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Keywords: 1,2-diaryldiazopropane; diazo compound; carbene reactions.

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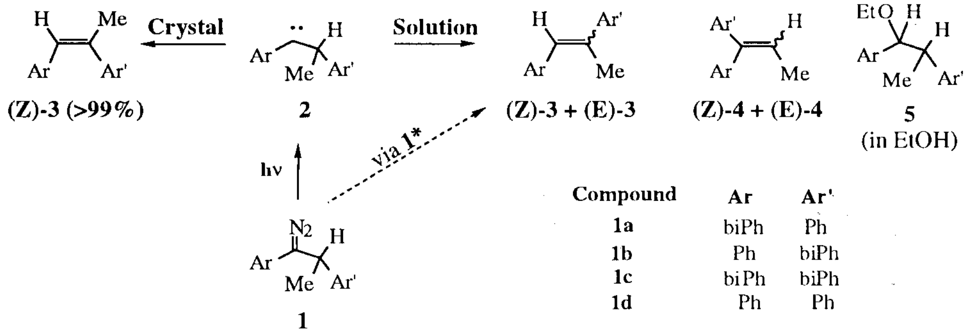


Compound	Ar	Ar'
1a	biPh	Ph
1b	Ph	biPh
1c	biPh	biPh
1d	Ph	Ph

Scheme 1.

proposed that carbene **2a** is generated in the solid state in a conformation that is essentially identical to that of **1a** so that product formation can be rationalized in terms of orbital alignment and reaction trajectories predicted by molecular orbital models.[29–31] A comparison between the X-ray structures of **1a** and **(Z)-3a** (Fig. 1, right side) supports a topochemical reaction where product formation occurs with minimum atomic displacement.

A straightforward implication of the results obtained with compound **1a** is that one should be able to predict the reactivity of diazo compounds and the selectivity of their carbene rearrangements if one can anticipate the conformation of the former. In order to test this simple concept, we have analyzed a set of diazo compounds that are closely related to compound **1a** but with small molecular and electronic structural variations given by phenyl and 4-biphenyl groups around the 1,2-diarylpropylidene frame (Scheme 2). Although the prediction of crystal structures is still a difficult task, it is known that neutral molecules tend to crystallize in their lowest energy conformations.[32] Based on that observation, *we expect that molecular structures in pure crystalline solids will be readily accessible from molecular mechanics with suitable force fields. With molecular structures at hand, we will be able to predict the outcome or reactions that are determined by conformational factors*. The validity of relatively simple calculations in the case of arylalkyldiazo compounds was recently supported by comparing the agreement between the calculated (MM3, Amber*, RHF/3-21G and RHF/6-31G* and B3LYP) and X-ray-determined structure of compound **1a**.[18,19] In order to test whether we can predict the selectivity of arylalkyl carbenes in crystals of compounds **1b–1d**, we carried out a set of molecular mechanics calculations with the Sybyl force field as implemented by MacSpartan with hopes of comparing those results with single crystal X-ray structures. To test our predictions, we also compared the selectivity of product formation in crystals of compounds **1a–1d** with each other and with results obtained in solution. The importance of homogeneity was analyzed by comparing the photochemical results obtained from crystals of **1a–1d** with results obtained in amorphous solids and dilute methylcyclohexane (MCH) glasses.

Results and Discussion

Diazo compounds

Racemic samples of diazo compounds **1b** and **1c** were obtained in good yields and high purity by yellow HgO oxidation[33] of the corresponding hydrazones as reported

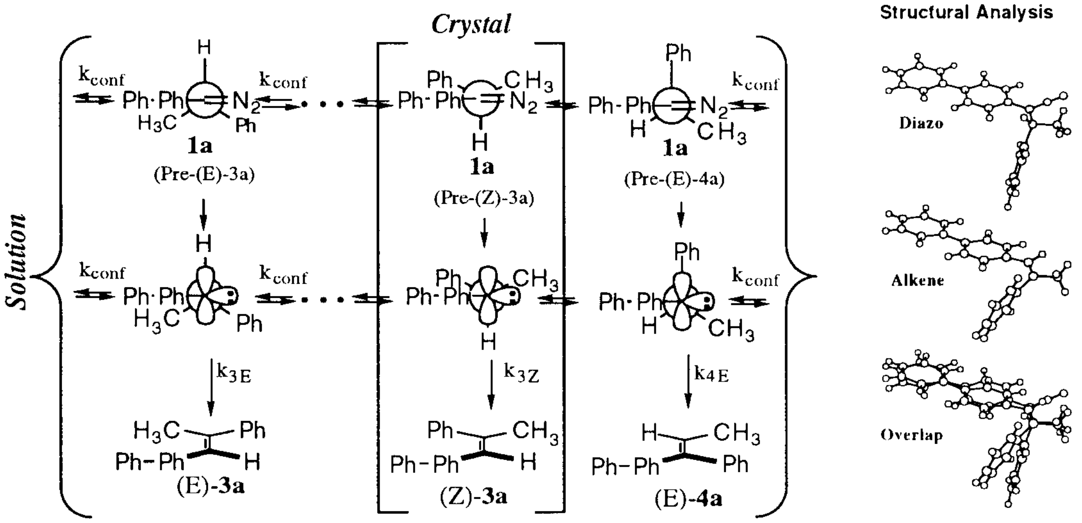
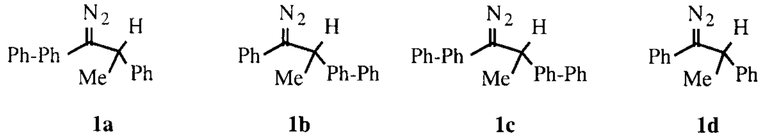


Figure 1. (Left) Schematic representation of the differences in conformational equilibration in solution and in the solid state. (Right) A comparison of the X-ray structures of Diazo **1a** and Alkene **(Z)-3a** illustrate the least motion nature of the solid state reaction.[17]



Scheme 2.

earlier for compounds **1a**[17] and **1d**.[34] The importance of properly selected excitation wavelengths in solid state reactions has been recently documented by several groups.[11,35] The UV–Vis spectra of compounds **1a**–**1d** (Scheme 2) in hexane solution have a nearly identical and very weak n,π^* absorbance in the visible (ϵ=40–50 L mol^{-1} cm^{-1} at $\lambda_{max}\approx$515 nm) but display significant differences in the strong π,π^* transitions in UV-region depending on whether a phenyl or a biphenyl group are conjugated with the diazo chromophore. The two compounds with conjugated biphenyl and diazo groups have similar spectra with λ_{max} at 318 and 514 nm for **1a** and at 322 and 516 nm for **1c**. Compounds **1b** and **1d** have λ_{max} at 285 and 513 nm. To insure photochemical reactivity in the bulk, excitation should be carried out at wavelengths where light is absorbed very weakly by the reactant and not at all by the products. After we determined that none of expected products (i.e. **3** and **4**) absorbs above 400 nm, we selected excitation wavelengths with λ>410 nm.

X-Ray analysis

Although samples for X-ray diffraction studies and photochemical experiments were crystallized by slow evaporation in pentane at 0°C, we unsuccessfully explored the formation of polymorphs by crystallization in a variety of solvents. The phase identity of samples used for reaction was confirmed by analysis of the fingerprint region of the solid state FTIR spectra measured in KBr dispersions. The molecular and crystal structures of **1a** (mp=94°C) as well as its solid state photochemistry have been described previously.[17] The molecular structure of **1a** is reproduced in Fig. 2 along with the structure of **1b**. A few experimental details are included in Table 1 for comparison with those that were either measured or calculated for the other compounds.[17] X-Ray diffraction of single crystals of **1b** (mp=82–84°C) revealed the formation of a pentane solvate in the cubic space group $P4_2/n$ with one diazo molecule per asymmetric unit. Studies that include solvates formed with other hydrocarbons and the details of data collection and refinement of **1b** will be reported elsewhere. The electronic density from disordered pentane molecules was located along a one dimensional channel parallel to the four-fold axis. As illustrated in Fig. 3, the 1D-channels are formed by translation of a supramolecular array of eight diazo molecules sharing aromatic face-to-face and face-to-edge interactions in a cyclic arrangement. The location of pentane molecules along the channel could not be determined, suggesting the possibility of rotational and translational disorder. Samples of **1c** were obtained as fine polycrystalline powders from several solvents and have a melting point between 112 and 116°C. Compound **1d**, which had been previously described as a non-crystallizable oil, was obtained as soft, low melting crystals (15–20°C), with poor diffraction quality.

Molecular mechanics

Molecular mechanics calculations with the Sybyl force field as implemented in MACSPARTAN[36] consistently predict that the lowest energy conformation of compounds **1b**–**1d** should be similar to that previously reported for **1a** (Fig. 2 and Table 1). The general features of the lowest energy conformers of **1a**–**1d** that are relevant to the chemical reactivity of the putative carbene intermediate are listed in Table 1 and may be described with reference to the side-by-side molecular mechanics and X-ray structures of compounds **1a** and **1b** (see Fig. 2). As expected for a delocalized π-system, molecular mechanics correctly predicts a nearly coplanar arrangement between the phenyl and diazo groups (i.e. Ph–CN$_2$) with a dihedral angle α=C21–C16–C15–N1 that is close to zero. The X-ray determined values are 4.7 and 2.1 for **1a** and **1b**, respectively. In a structural feature that is analogous to those of similar arylalkylketones where dipole-induced dipole interactions have been suggested,[37,38] we obtained a close to eclipsed conformation between the diazo group and the methyl substituent at the α-carbon. Dihedral angles β=C14–C13–C15–N1 of about 10° were calculated and measured for all the data set. As shown previously for **1a**, this particular conformation locates the hydrogen atom at the α-carbon (H13) relatively well aligned for a 1,2-H shift once the corresponding carbene is produced in the crystal lattice of the diazo compound. As illustrated in Scheme 3, it has been suggested that the sigma bond of the transferring hydrogen should be aligned with the empty orbital of the sp^2-hybridized singlet state carbene carbon.[30,39] This alignment stabilizes the carbene by hyperconjugation and locates the migrating group very near the transition state for the reaction. Assuming that the alignment in the structure of the diazo precursor will be maintained in

Table 1. Molecular mechanics and X-ray determined values of dihedral angles in compounds **1a**–**1d**

Diazo compound	α (C21–C16–C15–N1)		β (C14–C13–C15–N1)		γ (H13–C13–C15–N1)	
	Sybyl	X-Ray	Sybyl	X-Ray	Sybyl	X-Ray
1a	0	4.7	11.8	9.5	132.2	127.0
1b	0.02	2.1	12.2	11.9	132.7	130.6
1c	0.05	n.a.	11.7	n.a.	132.3	n.a.
1d	0.09	n.a.	11.6	n.a.	132.1	n.a.

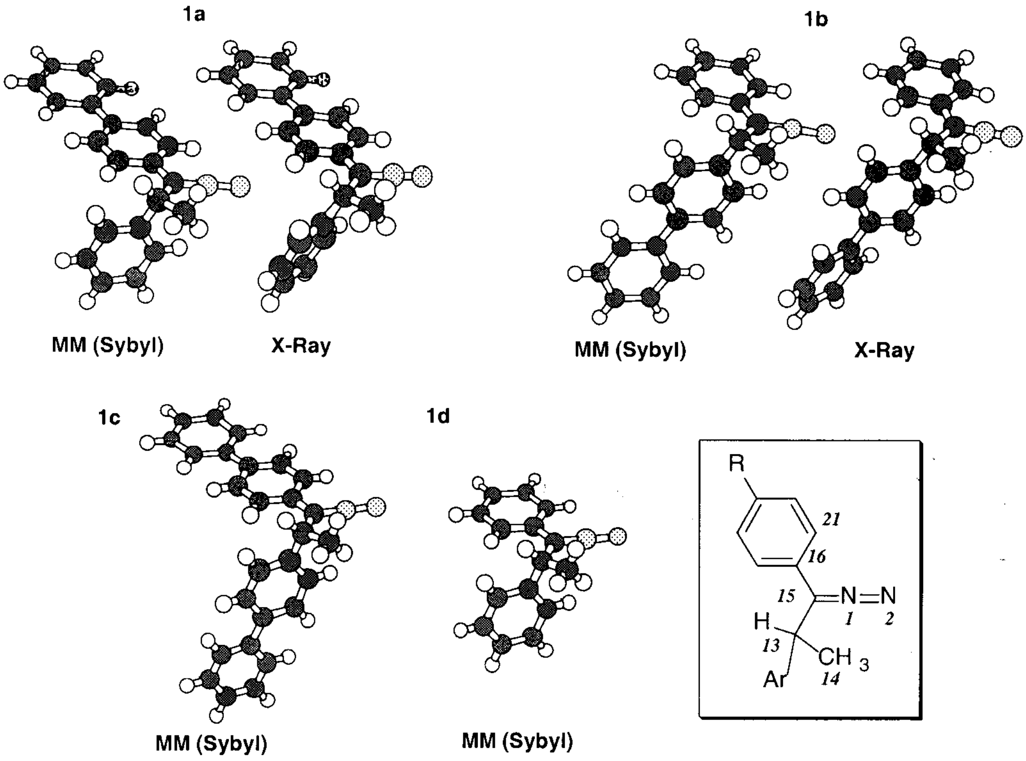


Figure 2. (Top) Comparison of molecular mechanics and X-ray structures of compounds **1a**[17] and **1b**. (Bottom) Molecular mechanics structures of **1c** and **1d**.

the carbene intermediate, one would hope for an ideal dihedral angle γ=H13–C13–C15–N1 of 90°. However, molecular mechanics of **1a**–**1d** and X-ray-determined structures of **1a** and **1b** indicate dihedral angles $\gamma \approx 130°$ which may slow down the rate of the reaction in the solid state. Although 1,2-H shifts in solution lead to (*Z*) and (*E*) alkenes with relatively low selectivities (see below), the lowest energy conformations of diazo compounds **1a**–**1d** should lead preferentially to carbenes that rearrange to give the (*Z*)-alkene isomers.

Solution photochemistry

It has been shown that solution photochemistry of 1,2-diaryldiazoalkanes is very sensitive to relatively small changes in structure, solvents and temperature.[25,40–44]

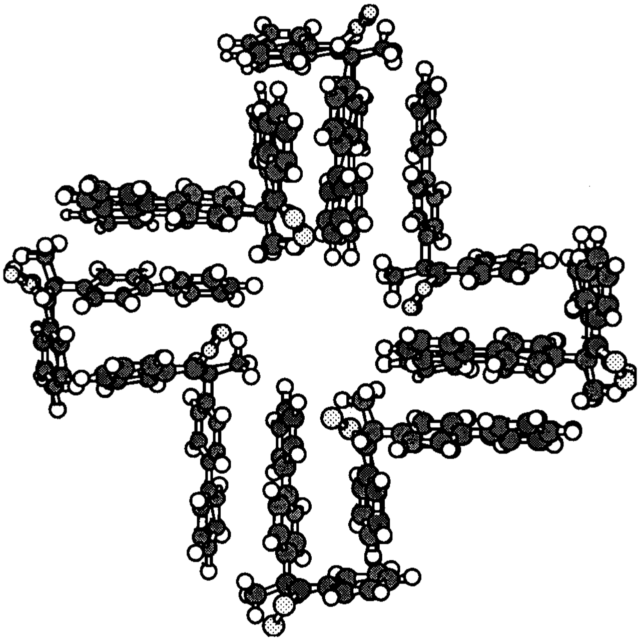
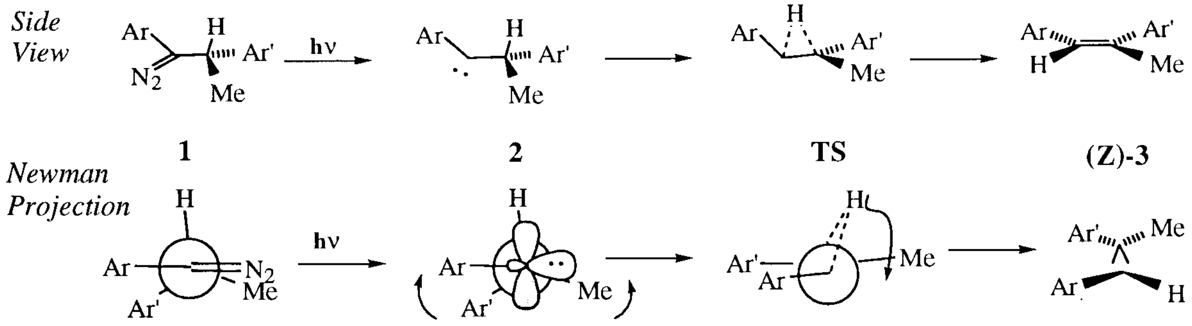


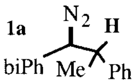
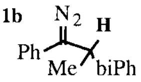
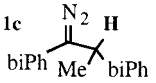
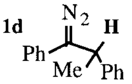
Figure 3. Cyclic octameric arrangement of diazo **1b** leading to formation of 1-dimensional channels along the four-fold axis. The location of pentane molecules along the channels could not be resolved.



Scheme 3.

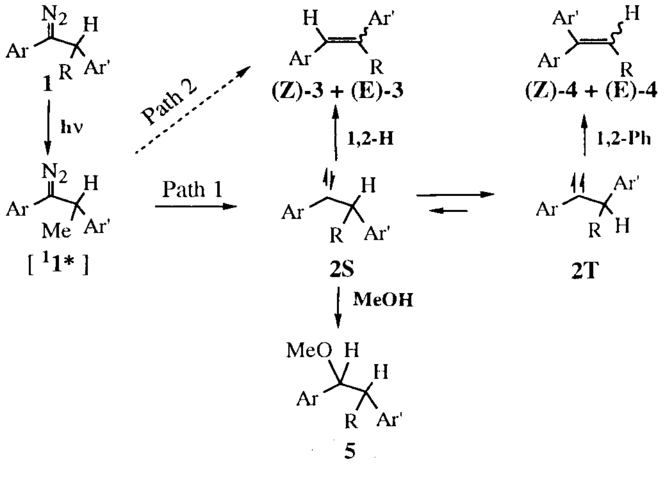
Carbene lifetimes of ca. 70–80 ns in fluorocarbon solvents[45] indicate reactions that occur with high pre-exponential factors and low activation energies. The results obtained with compounds **1a**–**1d** conform to that rule. Irradiations were carried out in dilute (10^{-3} M) deoxygenated hexane, acetonitrile, and ethanol solutions with $\lambda > 410$ nm in a thermostated bath at 0°C. The progress of the photochemical reaction was monitored by ^{1}H NMR or by gas chromatographic (GC) analysis at various time intervals. In order to prevent analytical interference by thermal formation of the carbene and its products under the conditions of analysis, partially reacted samples submitted to GC analysis were treated with sufficient dimethyl acetylenedicarboxylate (DMAD) to react with unphotolyzed diazo compound. The results of triplicate solution photolyses are shown in Table 2.

Table 2. Irradiation of 1,2-diaryldiazopropanes in various solvents with $\lambda > 400$ nm (the estimated uncertainty in relative product yields is ±10%)

Solvent	Diazo	**(*Z*)-3**	**(*E*)-3**	**(*Z*+*E*)-4**	**5**	**3/4**[a]
Hexane	**1a** 	16	10	74	n.a	0.35
MeCN		39	18	43	n.a.	1.32
EtOH		22	19	5	54	8.2
Hexane	**1b** 	23	15	62	n.a	0.61
MeCN		40	21	39	n.a.	1.56
EtOH		26	17	10	47	4.3
Hexane	**1c** 	21	3	76	n.a	0.32
MeCN		39	7	54	n.a.	0.85
EtOH		18	4	8	70	2.75
Hexane	**1d** 	41	31	28	n.a	2.57
EtOH		23	13	4	60	9.0

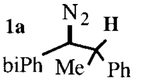
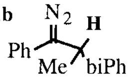
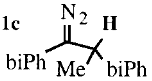
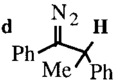
[a] Ratio of products [(*Z*)-**3**+(*E*)-**3**]/[(*Z*)-**4**+(*E*)-**4**].

Four alkenes from formal 1,2-H shifts [i.e. **(*Z*)-3** and **(*E*)-3**] and 1,2-Ph migrations [**(*Z*)-4** and **(*E*)-4**] illustrated in Scheme 4 accounted for more than 95% of the total photolysis mixture in hexane and acetonitrile. Irradiation of **1a–d** in ethanol resulted in high yields (ca. 50–70%) of ethyl ethers **5a–5d** by insertion of the carbene into the O–H bond. All products were identified by matching their gas chromatographic retention times with those of co-injected authentic samples. Compounds **(*Z*)-3a–d**, **(*E*)-3a–d**, and **5,** were independently synthesized, purified, and characterized, and samples of compounds **(*Z*)-4b–d** and **(*E*)-4b–d** were independently obtained as inseparable mixtures. The effects of structural changes and solvents of different polarities illustrated by the results in Table 2 can be understood in terms of a carbene intermediate (Scheme 4). However, as a note of caution, we have recently shown that excited diazo compounds such as **1** give free carbenes in yields that vary between 70–100% (Scheme 4, Path 1). Although a small amount of products may form directly by path 2, we have also shown that carbene yields increase with excitation at long wavelenghts.[44,45]



Scheme 4.

Table 3. Irradiation of 1,2-diaryldiazopropanes in crystalline and amorphous solids with $\lambda > 400$ nm (irradiations carried out to conversion values between 20 and 90%; yields are normalized)

Solid	Diazo	(*Z*)-3	(*E*)-3	(*Z*+*E*)-4	Insertion[a]
Cryst. 77, 273 K	**1a** 	>99	Trace	0	
Glass 273 K		51	29	20	
MCH 77 K		45	15	0	40
Cryst. 77, 273 K	**1b** 	>99	Trace	0	
Glass 273 K		61	32	7	
MCH 77 K		34	26	11	29
Cryst. 77, 273 K	**1c** 	>99	Trace	0	0
n.a.		–	–	–	
MCH 77 K		40	25	3	32
Cryst. 77, 273 K	**1d** 	85	15	0	
n.a.		–	–	–	–
MCH 77 K		59	2	7	32

[a] Mixture of products formed by reaction of the carbene with the MCH matrix. The estimated uncertainty in the values reported is less than 10%.

It is known that 1,2-diarylalkylidene possess a triplet ground state that exists in a very rapid equilibrium with the singlet state.[42,46] It is expected that 1,2-H shifts leading to **3** should occur from the singlet carbene (**2S**). However, strong experimental[40,42,43] and computational[47] evidence suggest that 1,2-Ph migrations to yield **4** should be competitive only if they can occur from the longer-lived ground state triplet (**2T**). We have suggested that carbene reactions in solution approach a state of pre-equilibrium where product yields reflect their rates of formation scaled by the fraction of carbenes in the spin state and conformation that is required for that particular reaction. An increase in the yield of **3** at the expense of **4** when the polarity of the solvent is increased from hexane to acetonitrile to ethanol has been taken as an indication of a shift in the spin state equilibrium from the neutral triplet to the polar singlet state. It is also known that an increase in solvent polarity can also affect the reaction selectivity by stabilization of the relatively polar 1,2-H transition state. High level computational studies provide evidence for both effects.[48]

Solid state photochemistry

Irradiations in the solid state were also carried out at $\lambda > 400$ nm in dilute methylcyclohexane glasses at 77 K, in amorphous solids of the neat diazo compounds at 273 K, and in pure polycrystalline samples at 77 and 273 K. The progress of the photochemical reaction was monitored by observing the decrease of the diazo band at 2033 cm^{-1} in KBr disks and by gas chromatographic (GC) analysis of samples drawn at various time intervals. Experiments in the solid state were carried out under three different conditions to analyze the effects of concentration, rigidity, and homogeneity (Table 3). *As expected from the combined use of conformational analysis by molecular mechanics and the accepted reaction mechanisms, nearly perfect reaction selectivities (up to >99%) with a clear preference for the Z-isomer of compounds* **3a**–**3d** *were observed when crystals of diazo compounds* **1a**–**1d** *were irradiated with* $\alpha > 400$ *nm either at 77 or 273 K.*

The selectivity in the crystalline solid state reflects not only the predisposition of the diazo compound and the intermediate carbene towards one of the products, but also the structural similarity between the initial and final structures in their lowest energy conformations. This can be illustrated by analysis of the X-ray structures of **1b** and **(Z)-3b** (Fig. 4). A similarity between the structures of the reactant and the product relates to the coplanar arrangement between the phenyl, diazo, and methyl groups in the reactant and a similar arrangement between the phenyl, alkene, and methyl groups in the product. As indicated by the arrows in the structure of the reactant shown in Fig. 4, the reaction in the solid state may be visualized by considering the accepted reaction mechanism (Scheme 3). In the first step of the reaction, nitrogen is extruded to form the carbene intermediate (arrow 1). It is expected that once formed within a crystal, carbenes will maintain the same overall conformation as the diazo compounds. While the lifetime of carbene **2b** in crystals of **1b** is not known at this time, it is likely to be significantly longer-lived than in solution. Notably, the transition states for 1,2-H shifts can be described as being relatively early with respect to the migrating hydrogen but late with respect to the formation of the double bond by planarization of the α-carbon. It may

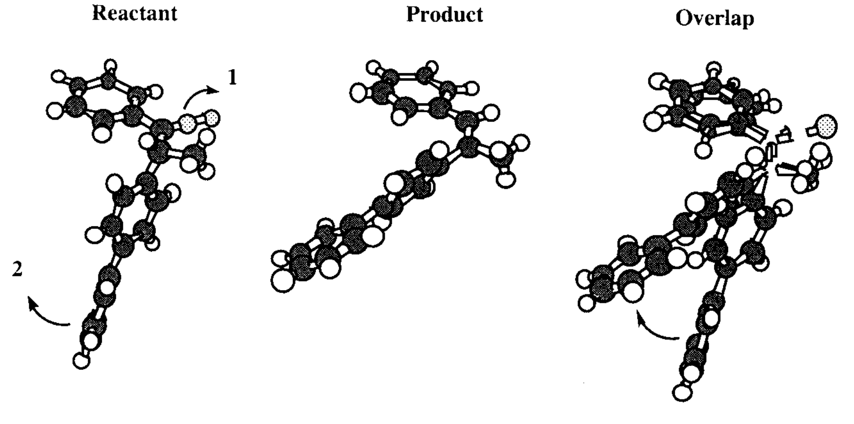
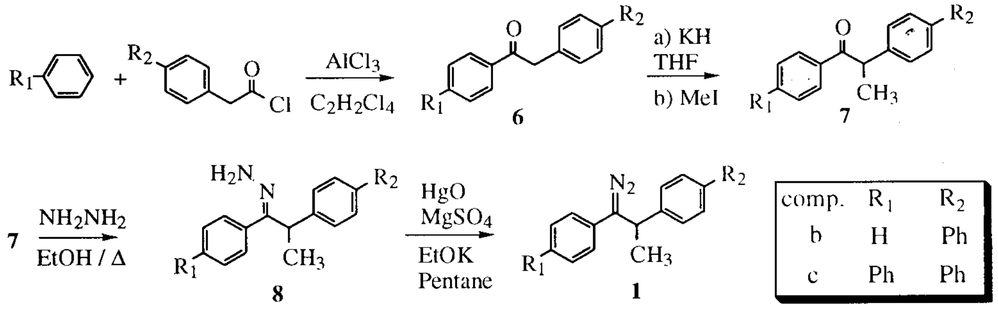


Figure 4.



comp.	R_1	R_2
b	H	Ph
c	Ph	Ph

Scheme 5.

be noted that rehybridization of the α-carbon in compound **1b** requires a substantial displacement of the biphenyl group (arrow 2), and it is likely that this displacement will be the rate limiting step in the solid state.

While excellent results were observed with crystals of compounds **1a–1c**, low melting (15–20°C) and poor quality crystals of 1,2-diphenyldiazopropane **1d** gave 85% of **(Z)-3a** and 15% of **(*E*)-3d**. In contrast, results with amorphous glasses of **1a** and **1b** clearly showed that rigidity without homogeneity is not enough to guarantee high reaction selectivities. Irradiation of amorphous samples produced by fast cooling yielded products from intramolecular 1,2-H shifts with preference for the (*Z*) isomers of alkenes **3a** and **3b** along with smaller amounts of products **4a–b** from 1,2-Ph migrations. We observed no traces of azine formation (R–N=N–R) despite generating the carbene in a medium where there is a high concentration of the diazo precursor. As a final point of comparison, irradiation of **1a–1d** in dilute MCH glasses at 77 K yielded product mixtures that are more complex than those observed in fluid solutions or in neat amorphous matrices. Stilbenes **3a–d** were obtained in 35–60% yields with small amounts of 1,1-diarylalkenes **4a–d** (0–20%), along with several products formed by reaction of the carbene with the methyl cyclohexane matrix (30–40% yields, Table 3).

For reactions in crystals to occur with high conversion values it is essential that reactants and products can coexist within the same phase over a wide range of compositions. We recently proposed that the transformation of crystals of **1a** into stilbene **(Z)-3a** can occur with maintained selectivity (>95%) to high conversion values (>95%) by formation of a metastable phase where the product retains the crystal structure of the reactant.[17] We have also suggested that efficient solid-to-solid reactions may occur, even in the event of a reconstructive phase separation process, when the solubility of the product in the phase of the reactant is sufficiently high, or when the newly formed phase can exert the same control as the parent phase on the selectivity of the reaction.[11] In general, it is expected that a high structural similarity between the molecular structures of the reactant and the product will facilitate the formation of solid solutions thus allowing for reactions to occur in high chemical yields.[11,23] Extended irradiation experiments with compound **1b** showed excellent selectivities to very high conversion values (ca. 80–90%). In analogy with our previous report on compound **1a**, the lack of a eutectic transition by differential scanning calorimetric analysis (DSC) suggests that the reaction proceeds along a single solid phase. Crystals of **1c** yielded **(Z)-3c** as the only product to conversion values as high as 20%. However, extended irradiation at 0°C resulted in a gradual decrease of the reaction selectivity. It appears that the structural changes caused by the displacement of two bulky biphenyl groups cannot be accommodated by the parent crystal structure and result in a detrimental disruption of the crystal lattice.

Conclusions

We have shown that the crystalline solid state may control the reactivity of aryldiazoalkanes to levels that have not been accomplished with any other media. We suggested that reaction control in the crystal derives from conformational factors that determine orbital alignment and from environmental factors that maintain a strong structural similarity between the reactant, the intermediate, the transition state and the final product. A comparison of the results obtained with crystals and amorphous solids confirms that rigidity without homogeneity is not enough to insure a high reaction selectivity. The results reported here suggest that the combined use of simple molecular mechanics and a detailed knowledge of reaction mechanisms may be robust enough to lead to the prediction of solid state reactivity.

Experimental

General

Reagents and solvents of the highest commercial purity were purchased from Fisher or Aldrich and were used as received. UV–Vis spectra were obtained on a Hewlett Packard 8453 UV–Vis spectrophotometer. IR spectra were acquired on a Perkin–Elmer Paragon 1000 FT-IR instrument. ^{1}H (^{13}C) NMR spectra were obtained on a Bruker AM360 broad band NMR spectrometer at 360 MHz (90 MHz) with $CDCl_3$ [7.24 (77.0)] or TMS [0 (0)] as internal standards. Gas chromatographic analyses (GC) were conducted on a Hewlett–Packard 5890 Series II capillary GC instrument equipped with a flame ionization detector (FID) and a Hewlett–Packard 3396 Series II integrator. An HP-1 (Crosslinked Methyl Silicone Gum) capillary column (25 m) with an inner diameter of 0.2 mm and a film thickness of 0.11 μm was used. Melting points were determined with a Fisher–Johns melting point apparatus.

Differential scanning calorimetry was performed on a Thermal Instruments DSC 2910.

Synthesis of diazo compounds

The synthesis of diazo compounds **1a** and **1d** has been reported before.[17] Compounds **1b** and **1c** were synthesized in a similar manner according to the sequence of reactions in Scheme 5.

Ketones 6b and 6c. Prepared by conventional Friedel–Crafts procedures as reported before in the synthesis of **1a** from biphenylacetyl chloride and benzene (**6b**), or biphenylacetyl chloride and biphenyl (**6d**). **2-(4′-Biphenylyl)-1-phenylethanone 6b**. ^{1}H NMR (360 MHz) δ: 4.31 (2H, s), 7.30–7.57 (12H, m, ArH), 8.02–8.04 (2H, m, ArH); ^{13}C NMR (90 MHz) δ: 45.0 (CH_2), 127.0, 127.2, 127.4, 128.6, 128.7, 129.9, 133.2, 133.5, 136,5, 139.8, 140.8 (Ar), 197.5 (C=O); FTIR (KBr Pellet) cm^{-1}: 3057, 3052, 2909, 1684, 1596, 1579, 1566, 1488, 1409, 1333, 1226, 1210. **1,2-Bis(4′-biphenylyl)ethanone 6c**. ^{1}H NMR (360 MHz) δ: 4.31 (2H, s), 7.23–7.48 (8H, m, ArH), 7.59–7.78 (8H, m, ArH), 8.07–8.19 (2H, m, ArH); ^{13}C NMR (90 MHz) δ: 45.5 (CH_2), 126.9, 127.2, 128.2, 128.7, 128.9, 129.2, 129.4, 134.6, 135.2, 139.8, 145.8 (Ar), 197.2 (C=O); FTIR (KBr Pellet) cm^{-1}: 3089, 3059, 3037, 3029, 2901, 1681, 1603, 1498, 1486, 1453.

Ketones 7b and 7c. Prepared by conventional alkylation procedures as reported before using NaH and MeI. **2-(4′-Biphenylyl)-1-phenylpropanone 7b**. ^{1}H NMR (360 MHz) δ: 1.55 (3H, d, J=6.8 Hz, CH_3), 4.71 (1H, q, J=6.8 Hz, CH), 7.20–7.45 (8H, m, ArH), 7.55–7.60 (4H, m, ArH), 8.01–8.04 (2H, m, ArH); ^{13}C NMR (90 MHz) δ: 19.5 (CH_3), 47.9 (CH), 126.9, 127.1, 127.2, 127.7, 128.1,128.9, 129.0, 129.3, 135.1, 139.8, 141.5, 145.4 (Ar), 199.8 (C=O); FTIR (KBr Pellet) cm^{-1}: 3084, 3067, 3027, 2982, 2975, 2932, 2673, 1605, 1497, 1453. **1,2-Bis(4′-biphenylyl)propanone 7c**. ^{1}H NMR (360 MHz) δ: 1.63 (3H, d, J=6.8 Hz, CH_3), 4.80 (1H, q, J=6.8 Hz, CH), 7.30–7.62 (14H, m, ArH), 7.64 (2H, d, J=8.3, ArH), 8.10 (2H, d, J=8.3, ArH); ^{13}C NMR (90 MHz) δ: 19.6 (CH_3), 47.6 (CH), 127.0, 127.2, 127.3, 127.3, 127.8, 128.3, 128.8, 129, 129.5, 135.2, 139.9, 140.6, 140.7, 145.5 (Ar), 199.9 (CO).

Hydrazones 8b and 8c. Prepared by refluxing ketones **7b** and **7c** with a 10 M excess of anhydrous hydrazine in ethanol as reported before. **2-(4′-Biphenylyl)-1-phenylpropanone hydrazone 8b**. ^{1}H NMR (360 MHz) δ: 1.51 (3H, d, J=7.1 Hz, CH_3), 3.92 (1H, q, J=7.1 Hz, CH), 5.10 (2H, s, NH_2), 6.96–7.00 (2H, m, ArH), 7.17–7.54 (12H, m, ArH); ^{13}C NMR (90 MHz) δ: 19.0 (CH_3), 47.5 (CH_2), 126.4, 126.9, 127.4, 127.5, 127.9, 128.2, 128.8, 132,9, 140.2, 141.10, 143.1 (Ar), 154.3 (C=N); FTIR (KBr Pellet) cm^{-1}: 3372 (N–H), 3268 (N–H), 3025, 2974, 2928, 2884, 1599, 1484, 1452. **1,2-Bis(4′-biphenylyl)propanone hydrazone 8c**. ^{1}H NMR (360 MHz) δ: 1.55 (3H, d, J=7.1 Hz, CH_3), 3.98 (1H, q, J=7.1 Hz, CH), 5.1 (br, 24), 7.03 (d, 2H, J=8.2 Hz, Ar-H), 7.25–7.60 (16H, m, Ar-H).

Diazo Compounds 1b and 1c. Diazo compounds were prepared from the appropriate hydrazone by yellow HgO oxidation as reported before. **2-(4′-Biphenylyl)-1-phenyldiazopropane 1b**. ^{1}H NMR (360 MHz) δ: 1.57 (3H, d, J=7.1 Hz, CH_3), 3.99 (1H, q, J=7.1 Hz, CH), 7.39 (10H, m, ArH), 7.60 (4H, m, ArH); ^{13}C NMR (90 MHz) δ: 20.9 (CH_3), 34.7 (CH), 61.2 ($C{=}N_2$), 122.2, 126.6, 126.8, 126.9, 127.6, 128.7, 128.8, 130.1, 136.2, 140.5, 144.1 (Ar); FTIR (KBr Pellet) cm^{-1}: 3081, 3066, 3029, 2971, 2939, 2874, 2033 ($C{=}N_2$), 1683, 1604, 1557, 1518, 1487, 1455. **1,2-Bis(4′-biphenylyl)diazopropane 1c**. ^{1}H NMR (360 MHz) δ: 1.58 (3H, d, J=7.1 Hz, CH_3), 4.04 (1H, q, J=7.1 Hz, CH), 6.99 (2H, d, J=8.6 Hz, Ar-H), 7.25–7.65 (16H, m, Ar-H); ^{13}C NMR (90 MHz) δ: 20.8 (CH_3), 34.4 (CH), 61.5 (CN_2), 122.2, 126.6, 127.0, 127.2, 127.3, 127.6, 128.7, 130.2, 136.3, 139.8, 140,5, 140.7, 143.2 (Ar); FTIR (KBr Pellet) cm^{-1}: 2035 cm^{-1} (CN_2).

Solution photolysis

Approximately 1 mg of **1** was dissolved in 1 mL of solvent. The solution was placed in an NMR tube and Ar gas was bubbled through the solution for 20 min to deoxygenate the sample. Photolysis was carried out in an ice bath (0°C) with a 410 nm cutoff filter. Samples were irradiated for 30 min after which the characteristic red color of **1** had disappeared. Upon completion of photolysis, dimethyl acetylenedicarboxylate (DMAD) was added to react with any remaining **1**. GC analysis revealed the composition of the product mixture and the results are shown in Table 2.

Microscale solid state photolysis

Samples of 20 mg of **1** were ground into fine powders and mixed with 5 mg of ground crystals of triphenyl methanol which served as a standard to determine extent of conversion. Powdered samples were placed between two microscope slides in a polyethylene bag immersed in an ice bath (0°C). Photolyses were performed with a 410 nm cutoff filter. Approximately 1 mg of the irradiated sample was removed for analysis every 15–60 min. The removed portions were dissolved in diethyl ether, DMAD was added, and the resulting solutions analyzed by GC (Table 3). Microscale photolysis were also carried out with amorphous solid samples. Samples were prepared by melting 5 mg of crystalline **1** followed by fast cooling under liquid N_2. The glassy material thus obtained was sandwiched between two microscope slides, irradiated for about 3 h in an ice bath (0°C) with the 410 nm filter, and analyzed.

Medium scale solid state photolysis

Samples of 50–100 mg of **1a**–**1d** were ground into a fine powder. This powder was placed on a watch glass and covered with a 410 nm filter. At varying time intervals (60 min) irradiation was stopped and the sample removed for DSC (5 mg), solid state FT-IR (1 mg) and GC (1 mg) analysis.

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