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Photolysis of an asymmetrically substituted diazene in solution and in the crystalline state†‡

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In this work we study the product distribution in the steady state photolysis of a diazene, (1-biphenyl-4-yl-1-methyl-ethyl)-*tert*-butyl diazene, and a ketone, 2,4-bis(biphenyl-4-yl)-2,4-dimethyl-pentan-3-one, in the solid state and in solution. The two compounds yield 1-biphenyl-4-yl-1-methyl-ethyl (BME[•]) radicals upon photolysis. The ketone yields two units of this radical, whereas the diazene yields one BME[•] and one *tert*-butyl radical. Product analysis of the two compounds in solution makes it possible to differentiate their origin from their corresponding geminate cages, and from the different encounter pairs in the case of the asymmetrically substituted diazene photolysis. In this way we obtain a complete reaction scenery for the diazene, a compound with interesting features as a radical photoinitiator and as a cage effect probe in fluid media. The reaction in cages containing two BME[•] radicals shows a decrease by a factor of 4 in the ratio of combination to disproportionation products upon going from the solid to the liquid phase. On the contrary, the reaction in cages containing a BME[•] and a *tert*-butyl radical shows a 30-fold increase in combination to disproportionation ratio in liquid compared to the crystal. We analyze the reasons for these differences considering the differences in the reactivity of the radicals and in cage rigidity.

Introduction

Azoalkanes, also known as diazenes, are characterized by the presence of two double-bonded nitrogens linked to saturated carbon atoms. Diazenes have been studied extensively due to their application as photoinitiators in radical polymerization reactions.¹ Their most characteristic reaction pathway involves the loss of N₂ by stepwise cleavage of the two N–C bonds to yield a singlet radical pair.^{2,3} While the reaction occurs both thermally and photochemically, the excited state reaction often competes with *E-Z* isomerization,^{2,4} unless the latter is greatly disfavored by bulky groups on the two α -carbons.

Cage effects in radical reactions have attracted attention due to their effect in the production of diffusive free radicals, and because of their utility as chemical probes for confinement effects. While reactions of ketones have been used for this purpose extensively,

most of them occur in the triplet state and produce diffusive free radicals that react by random encounters.⁵ In contrast, the loss of N₂ from diazenes occurs from the singlet manifold and in sub-picosecond timescale;⁶ geminate radical pairs are more likely to react within the solvent cage. For that reason, diazenes may be suitable probes for cage effects in weakly structured fluids, such as supercritical fluids and compressed gases, where most ketones would lead to products that arise from diffusion-mediated radical–radical reactions.⁷ The evaluation of the cage effect by product distribution can be more easily solved if compounds rendering two different radicals upon dissociation are used.⁸ Moreover, if transients are used for this same purpose, it would be highly desirable to design a compound yielding easily traceable intermediates.

For this work, we have synthesized (1-biphenyl-4-yl-1-methylethyl)-*tert*-butyldiazene (BTD, Chart 1) with a *tert*-butyl

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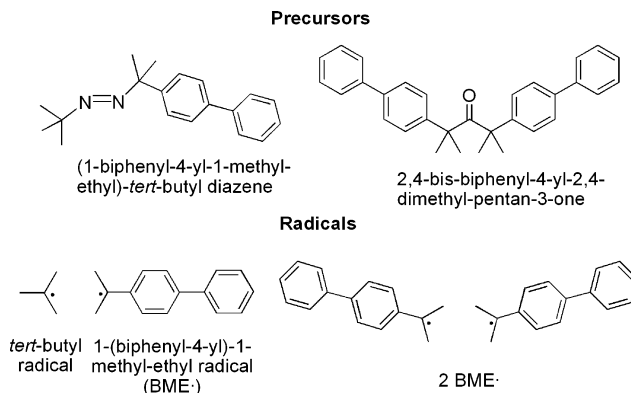


Chart 1 Structures of the diazene, ketone and radical intermediates.

group bound to one N and a chromophoric biphenyl bound to the other. While simple azoalkanes have low absorption coefficients, the strongly absorbing biphenyl acts as an antenna with an absorption coefficient exceeding $2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 254 nm. As the methyl substituents at the two alpha carbons prevent an observable *E-Z* isomerization, a relatively high quantum yield of dissociation of 0.38 in cyclohexane is obtained for BTD.

Dissociation of the diazene yields *tert*-butyl and 1-biphenyl-4-yl-1-methyl-ethyl (BME[•]) radicals. BME[•], having benzyl nature,⁹ is expected to display favorable features for detection by differential absorption laser flash photolysis. To have an alternative and exclusive source of BME[•], we synthesized 2,4-bis(biphenyl-4-yl)-2,4-dimethyl-pentan-3-one, which also served to characterize the reactivity of BME[•] radicals in solution. Diazene and ketone structures, as well as the radicals they produce after photolysis and loss of either nitrogen or carbon monoxide, are shown in Chart 1.

Photochemical reactions were explored in solution and in the solid state. Radical pairs generated in diazene crystals may be viewed as an extreme case of in-cage reactions. However, radical-radical reactions may be subject to specific crystal packing effects so that they may have different outcomes in different crystals. While radical pairs derived from ketones tend to give combination products, McBride and collaborators observed a large amount of disproportionation products (50–95%) in the photolysis of several crystalline diazenes.^{10,11} In the photolysis of solid 2,2'-azobis(2-methylpropionitrile) (AIBN) and 2,2'-azobis(2-cyanopropanol) (ACP) they observed no more than 5% of disproportionation products in solution and about 95% in the solid state. They reported melting of the crystal upon completion of photolysis. These studies comprise compounds with structurally similar residues on both sides of the nitrogen–nitrogen double bond.^{10,12} Asymmetrically substituted diazenes in the solid state are found in the literature, but no studies on the photolysis in the solid is described in such cases.¹³ Considering that the solid environment has such a crucial influence in the branching of disproportionation to combination, we decided to study also the solid state photolysis of an asymmetrically substituted compound to observe the influence of different H-abstraction capabilities in the mentioned competing reactions. To determine the influence of energetic and entropic factors, we performed temperature dependent studies in the solid state.

In this article we report the solid state photolysis of an asymmetrically substituted diazene with a biphenyl moiety over a broad temperature range. The results obtained from these studies enable us to estimate the activation energy and entropy difference of the competing processes. We also report a complete product distribution analysis to evaluate quantitatively their origin as arising from reactions between geminate or out-of-cage radical pairs in solution. This characterization is significant for applications based on the use of the diazene as a probe of the cage effect by product analysis.

Experimental

Synthesis of (1-biphenyl-4-yl-1-methyl-ethyl)-*tert*-butyl diazene

The synthesis of asymmetrically substituted diazenes is found in the literature.¹⁴ The synthesis is done beginning with an alcohol and an amine.

Synthesis of 1-biphenyl-4-yl-1-methyl-ethylamine 1. The amine was synthesized starting from 4-biphenyl-carbonitrile (6.11 g, 34.1 mmol) by addition of (CH₃)CeCl₂ (105 mmol, prepared *in situ* by mixing methyl lithium, 75 ml of 1.4 M solution, and anhydrous CeCl₃, 40 g, in dry THF), according to the procedure described by Ciganek.¹⁵ The residue obtained on removal of CH₂Cl₂ from the dried (MgSO₄) extracts was purified by column chromatography on silica using CH₂Cl₂ as eluant until the imine (single methylation by-product) was removed and then with 5% CH₃OH in CH₂Cl₂ to yield **1** (4.8 g, 66%) after removal of solvent. δ_{H} (400 MHz; CDCl₃; Me₄Si) 1.54 (s, 6 H, 2 × CH₃), 7.3–7.64 (m, 9 H, Ph-Ph); *m/z* (EI) 211.1366 (M⁺, C₁₅H₁₇N requires 211.1361).

Synthesis of *tert*-butyl-sulfamoyl chloride 2. *tert*-Butanol (5.25 g, 70 mmol) was dissolved in 42 ml of hexanes followed by dropwise addition in a 30 min period at room temperature of 10.15 g of chlorosulfoisocyanate dissolved in 21 ml of hexanes.¹⁶ The mixture was heated 20 min at 50 °C to complete the decarboxylation process. The solution was rotavaped leaving a liquid behind. δ_{H} (400 MHz; CDCl₃; Me₄Si) 1.48 (s, 9 H, 3 × CH₃).

Synthesis of (1-biphenyl-4-yl-1-methyl-ethyl)-*tert*-butyl-sulfamide 3. The amine **1** prepared before (4.8 g, 22.7 mmol) was dissolved in 12.3 ml of anhydrous diethyl ether and 2.93 g of di-isopropyl-ethylamine were added. The solution was then added dropwise under Ar at 0 °C to a solution of **2** (22.7 mmol) in 43 ml of anhydrous diethyl ether. The mixture was then left at room temperature for 3 h with continuous stirring. The reaction was finished by adding water to the solution. The organic layer was discarded and the obtained solid was filtered, washed and dried to give **3** (34%) as a pale white solid. The yield should be increased if more mass of **2** is used. δ_{H} (400 MHz; CDCl₃; Me₄Si) 1.28 (s, 9 H, 3 × CH₃), 1.77 (s, 6 H, 2 × CH₃), 3.74 (s, 1 H, NH), 4.47 (s, 1 H, NH), 7.3–7.63 (m, 9 H, Ph-Ph).

Synthesis of (1-biphenyl-4-yl-1-methyl-ethyl)-*tert*-butyl diazene 4. A suspension of 2.65 g of **3** in 24 ml of an aqueous solution of NaOH 10% (about 8 equivalents) was prepared and a similar volume of hexanes was added. Over a 45 min period 88 ml of a solution of NaClO 5% was added dropwise while keeping the mixture in an ice/water bath. The reaction was left overnight. The aqueous layer was extracted twice with hexanes and the combined organic layers were dried and rotavaped. The product was purified by column using a mixture of hexanes:CH₂Cl₂ of 4:1 as eluant, giving **4** (47%) as a pale yellow solid (Found: C, 81.3 ± 0.3; H, 8.7 ± 0.2; N, 9.9 ± 0.3. Calc. for C₁₉H₂₄N₂: C, 81.4; H, 8.6; N, 10.0%; λ_{max} (cyclohexane)/nm 254 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 20 500) and 365 (75 ± 5); δ_{H} (400 MHz; CDCl₃; Me₄Si) 1.23 (s, 9 H, 3 × CH₃), 1.49 (s, 6 H, 2 × CH₃), 7.27–7.65 (m, 9 H, Ph-Ph); δ_{C} (100 MHz; CDCl₃; Me₄Si) 26.6, 26.8, 66.7, 70.6, 126.6, 126.9, 127.1, 128.7, 139.3, 141.0, 145.6.

Crystal structure determination of 4

Crystal data. C₁₉H₂₄N₂, *M* = 280.40, orthorhombic, *a* = 5.9800(7), *b* = 8.0417(10), *c* = 33.922(4) Å, *U* = 1631.3(3) Å³, *T* = 120(2) K, space group *P*2₁2₁2₁ (no. 19), *Z* = 4, 14 614 reflections measured,

3902 unique ($R_{\text{int}} = 0.0705$) which were used in all calculations. The final wR_2 was 0.1093 (all data).

Synthesis of 2,4-bis(biphenyl-4-yl)-2,4-dimethyl-pentan-3-one

Synthesis of 1,3-bis(biphenyl-4-yl)-propan-2-one 5. The synthesis of the symmetric ketone using biphenyl-acetic acid as starting material was analogous to the procedure followed by Bhandari and Ray,¹⁷ with some variations introduced by Sauriat-Dorizon *et al.*¹⁸ Because biphenyl-acetic acid is not completely soluble in CH_2Cl_2 , a suspension of the acid (7.0 g, 33.0 mmol) in 100 ml CH_2Cl_2 was added dropwise to the solution of 1,3-dicyclohexylcarbodiimide (6.8 g, 33.0 mmol) and 4-dimethylaminopyridine (1.01 g, 8.24 mmol) in 50 ml of the same solvent. The reaction was left at room temperature for 44 h and then ethanol was added until the solid was dissolved at the boiling point (some CH_2Cl_2 was added to complete solubilization of the mixture). Crystallization from this solvent mix gave polymorph A of **5** (61%). Recrystallization of the solid in ethyl acetate gave polymorph B. Mp 153–162 °C (from dichloromethane–ethanol by DSC) and 152–158 °C (from ethyl acetate by DSC) (lit.,¹⁹ 146–148 °C from ethanol); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 1713 (CO, from dichloromethane–ethanol) and 1700 (CO, from ethyl acetate) (lit.,¹⁹ 1720, from ethanol); δ_{H} (500 MHz; CDCl_3 ; Me_4Si) 3.79 (s, 4 H, $2 \times \text{CH}_2$), 7.22–7.57 (m, 18 H, $2 \times \text{Ph-Ph}$) (lit.,¹⁹ non-aromatic singlet at 3.77); δ_{C} (125.8 MHz; CDCl_3 ; Me_4Si) 48.8, 127.0, 127.3, 127.5, 128.8, 129.9, 133.0, 140.1, 140.7, 205.6.

Synthesis of 2,4-bis(biphenyl-4-yl)-2,4-dimethyl-pentan-3-one 6. The permethylation of **5** was performed based on the work of Millard and Rathke.²⁰ Due to the difference in solubilities between the ketone in use and the ones published, additional THF is used to prepare the ketone solution and then is added to the KH (1.28 g, 32 mmol) suspension in THF (15 ml). Five minutes after the addition of the ketone (1.0 g, 2.76 mmol), 11 equivalents of methyl iodide were added dropwise. The reaction mixture was left 15–20 min at room temperature and then refluxed for an hour. After cooling the reaction mixture in an ice/water bath, about 1.5 equivalents of methyl iodide were added. The mixture was left at room temperature for an hour and then quenched with water. The suspension was filtered and the solid, washed with cold methanol. Extraction from the aqueous layer with two portions of ethyl ether (3 ml each) and combination of organic layers yielded more product after drying over anhydrous K_2CO_3 and rotavaping, obtaining **6** (91%) as a pale yellow solid. mp 201.5–207.6 °C (by DSC); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 1686 (CO); δ_{H} (400 MHz; CDCl_3 ; Me_4Si) 1.37 (s, 12 H, $4 \times \text{CH}_3$), 7.19–7.56 (m, 18 H, $2 \times \text{Ph-Ph}$); δ_{C} (100 MHz; CDCl_3 ; Me_4Si) 28.0, 52.9, 126.4, 126.8, 126.9, 127.2, 128.8, 139.1, 140.5, 143.3, 213.4.

Crystal structure determination of 6

Crystal data. $\text{C}_{31}\text{H}_{30}\text{O}$, $M = 418.57$, monoclinic, $a = 8.1279(9)$, $b = 6.3065(7)$, $c = 22.035(2)$ Å, $\beta = 97.416(2)^\circ$, $U = 1120.0(2)$ Å³, $T = 120(2)$ K, space group $P2_1/n$ (no. 13), $Z = 2$, 9614 reflections measured, 2720 unique ($R_{\text{int}} = 0.0529$) which were used in all calculations. The final wR_2 was 0.1108 (all data). This molecule has crystallographically imposed two-fold symmetry with the carbonyl group on the two-fold axis.

Synthesis of the products of photolysis of (1-biphenyl-4-yl-1-methyl-ethyl)-tert-butyl-diazene

Synthesis of 1,1'-bis(1-biphenyl-4-yl-1-methyl-ethyl) (biBME) 7. A solid sample of **6** was irradiated for 50 h with a Hannovia lamp 400 W. NMR data shows about 50% conversion to the decarbonylated product. The product was purified by column chromatography using hexanes as eluant until the first compound was eluted. Then the unreacted ketone was recovered eluting with ethyl acetate. After evaporating the appropriate fractions under reduced pressure a yellow solid amount of **7** is obtained. Mp 220.7–223.5 °C; δ_{H} (400 MHz; CDCl_3 ; Me_4Si) 1.36 (s, 12 H, $4 \times \text{CH}_3$), 7.14–7.61 (m, 18 H, $2 \times \text{Ph-Ph}$); m/z (FAB) 195.1 (100%, $\text{M} - \text{C}_{15}\text{H}_{15}$), 237.4 (36, $\text{M} - \text{C}_{12}\text{H}_5$).

Synthesis of 4-(1,1,2,2-tetramethyl-propyl)-biphenyl (TMPB) 8. A sample of **4** was dissolved in 200 ml of benzene, and was irradiated for 1.5 h in an immersion well with a Hannovia lamp 400 W. The mixture was purified by column chromatography using hexanes as eluant obtaining fractions of pure disproportionation products, and fractions of mixed disproportionation and combination products. Colorless solid plates of **8** are obtained after evaporation of the eluant. $\lambda_{\text{max}}(\text{cyclohexane})/\text{nm}$ 254 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 18 500) (lit.,²¹ 20 500, 95% ethanol); δ_{H} (400 MHz; CDCl_3 ; Me_4Si) 0.88 (s, 9 H, $3 \times \text{CH}_3$), 1.39 (s, 6 H, $2 \times \text{CH}_3$), 7.30–7.63 (m, 9 H, Ph-Ph) (lit.,²¹ 0.87 (s, 9 H), 1.39 (s, 6 H), 7.3–7.7 (m, 9 H).

Synthesis of 4-isopropenyl-biphenyl (i-PenB) 9. A sample of 150 mg of **6** was dissolved in 200 ml of benzene, and was irradiated for 1.5 h in an immersion well with a Hannovia lamp 400 W, being continuously bubbled with nitrogen. The conversion was complete, showing by NMR a ratio of products 1.4: 1 of **7** to **9**. The mixture was purified by column chromatography using hexanes as eluant obtaining fractions of pure **7**, fractions of mixed disproportionation products and fractions of pure disproportionation products, liquid 4-isopropyl-biphenyl and solid **9**. δ_{H} (400 MHz; CDCl_3 ; Me_4Si) 2.20 (dd, 3 H, $J = 0.72, 1.4$ Hz, $\text{CH}_3\text{C}=\text{CH}_2$), 5.13 (quintet, 1 H, $J = 1.4$ Hz, $\text{CH}_3\text{C}=\text{CH}_A\text{H}_B$), 5.45 (q, 1 H, $J = 0.72$ Hz, $\text{CH}_3\text{C}=\text{CH}_A\text{H}_B$), 7.33–7.63 (m, 9 H, Ph-Ph); δ_{C} (100.6 MHz; CDCl_3 ; Me_4Si) 21.8, 112.4, 125.9, 126.9, 127.0, 127.2, 128.8, 140.1, 140.2, 140.7, 142.7.

Steady state irradiation, product distribution, and actinometry

The diazene solid plates were obtained by crystallization from diethyl ether. The plates were placed in a closed NMR tube and photolyzed using a Nd:YAG laser at 355 nm (10 Hz, 8 ns FWHM pulses, 10 mJ per pulse). After photolysis, the lower portion of the tube was cooled under liquid nitrogen to prevent loss of volatile compounds of interest. Chloroform was then added. The sample was analyzed by HPLC (LichroCart RP-18 5 μm , 250×4.6 mm), eluting with methanol–water 0.89:0.11 at 1 ml min^{-1} flux. Each sample was injected twice, first with detection at 254 nm and afterwards at 272 nm. This procedure serves to discriminate the composition of the co-eluting compounds in the first peak, 4-isopropyl-biphenyl and 4-isopropenyl-biphenyl. Photolysis experiments were performed from liquid nitrogen to above room temperature at various temperatures, which was controlled by placing the NMR tube containing the sample in a Dewar with quartz windows, that contained a cooling bath. This

was liquid nitrogen for 77 K and liquid nitrogen cooled solvents for other cryogenic temperatures (petroleum ether, ethanol or acetone were used). The sample was allowed to equilibrate in the Dewar for about 20–30 min prior to irradiation. Temperatures between 77 K and 175 K could not be attained, as there was no appropriate solvent to achieve them. Samples were irradiated to 35–80% diazene degradation.

In the photolysis experiments in cyclohexane solution, the product distribution was analyzed by HPLC after irradiation of the diazene at 365 nm and of the ketone (see below) at 254 nm. Irradiations were performed at 254 nm using a low pressure Hg lamp (Philips TUV 4 W) and at 365 nm using a LED (UVLED365–10 Roithner Lasertechnik, Wien, Austria). Quantum yields for disappearance of diazene were measured by using the isomerization of azobenzene as an actinometric reference.^{22–25} Azobenzene (J. T. Baker) in methanol (Sintorgan HPLC grade) at a concentration of *ca.* 6×10^{-4} M was used. For actinometry at 254 nm the azobenzene solution was pre-irradiated up to the photostationary state with the 365 nm light source and *vice versa*. Photolysis with 254 nm light was performed using WG225 filters when needed to adequately attenuate light intensity. Once the photon flux is known, quantification of diazene disappearance (and product distribution at 365 nm irradiation) was performed by HPLC analysis (same conditions as above, but eluting with methanol–water 0.80 : 0.20 at 1 ml min⁻¹ flux).

Product analysis and quantification by HPLC

The elution order was confirmed by injection of pure product samples. NMR data of all expected products serve as qualitative and quantitative information. Simultaneous analysis by HPLC and NMR integration of ¹H gave the same amounts of products formed during the photolysis, validating HPLC measurements for routine analysis. *i*-PenB has a maximum absorption wavelength shifted to the red (272 nm), compared to the *i*-PB maximum (252 nm). Detection at two wavelengths (around the maximum absorption of each of the co-eluting products) serves to quantify them by solving a two equations system.

Molecular modeling

DFT computational calculations were carried out using the Gaussian 98 package²⁶ using 6-31G** basis set and a B3LYP functional *in vacuo*, to optimize geometries for the diazene and its primary formed radicals, as well as all of its expected combination and disproportionation products inside the cage.

Results

The absorption spectrum of the diazene consists of the highly absorbing biphenyl π, π^* band and the weak diazo n, π^* band. These bands have their maximum absorption at 254 nm ($\epsilon = 2.05 \pm 0.05 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and at 365 nm ($\epsilon = 75 \pm 5 \text{ M}^{-1} \text{ cm}^{-1}$), respectively. The π, π^* band of the diazo group would be submerged into the substantially bigger biphenyl absorption band. The ketone has a maximum at 259 nm overlapping also with the biphenyl absorption. The n, π^* band is hidden under this absorption and is assumed to peak around 280–290 nm.

Chart 2 illustrates the structures of the expected products after photolysis. Among them, 4-(1,1,2,2-tetramethylpropyl)-

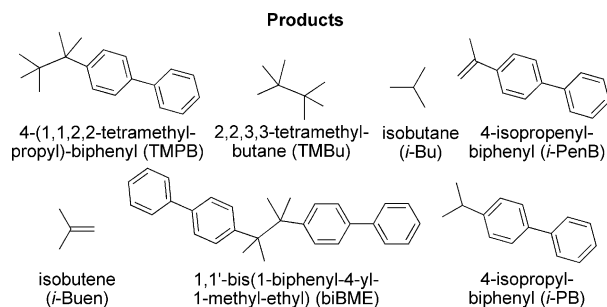
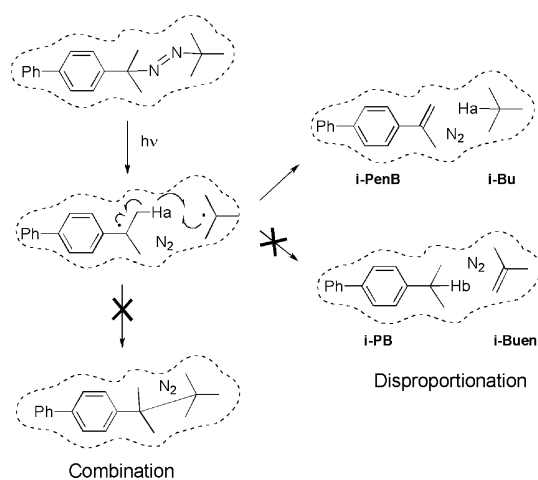


Chart 2 Structures of the photolysis products.

biphenyl (TMPB), 2,2,3,3-tetramethylbutane (TMBu) and 1,1'-bis(1-biphenyl-4-yl-1-methyl-ethyl) (biBME) are formed by radical–radical coupling reactions. In contrast, 4-isopropenylbiphenyl (*i*-PB), isobutene (*i*-Buen), 4-isopropenylbiphenyl (*i*-PenB) and isobutane (*i*-Bu) are formed by radical–radical disproportionation.

Photochemistry in the solid state

Crystals of the ketone exclusively led to the radical–radical coupling product biBME, while irradiation of diazene crystals to low conversion and analysis by ¹H NMR and HPLC indicated the predominant formation of disproportionation products. While there are two possible disproportionation pathways for the diazene-derived BME–*tert*-butyl radical pair, we found that *i*-PenB+*i*-Bu is preferred to formation of *i*-PB+*i*-Buen by a >20 : 1 ratio. This result is consistent with the lower bond dissociation energy of Ha (Scheme 1), the hydrogen atom in alpha to the radical center in BME*, as compared to the analogous hydrogen in the *tert*-butyl radical. This is manifested in the relative stability of the resulting products as shown by DFT calculations indicating that the energy of formation of *i*-PenB+*i*-Bu is 7.64 kJ mol⁻¹ lower than that of *i*-PB+*i*-Buen. Product analysis as a function of conversion at 298 K confirmed that product accumulation does not lower the selectivity of the reaction up to *ca.* 70% conversion (Fig. 1). These results suggest that variations in the crystals as a function



Scheme 1 Disproportionation and combination pathways for the BME–*tert*-butyl radical pair in crystals of their diazene precursor. The reaction cavity formed by close neighboring molecules in the crystal lattice is illustrated with a dotted line.

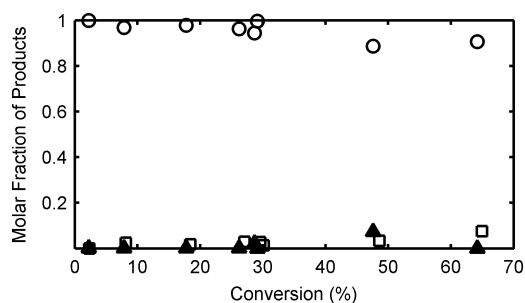


Fig. 1 Product distribution in the photolysis of the diazene in the solid state as a function of conversion at room temperature. Circles, squares and triangles represent disproportionation, combination, and unknown products, respectively.

of product accumulation are well tolerated by the solid sample. A relatively small amount of TMPB and the lack of biBME and TMBu suggest that radical reaction occurs with 100% cage effect, as expected for reactions occurring within the rigid reaction cavities of molecular solids.

In order to gain insight into the parameters that affect the solid state reaction we carried out a series of photolysis experiments as a function of temperature between 77 and 320 K. A small variation in the product distribution was observed in the range of 170–320 K, and a surprising decrease in the reaction selectivity observed at 77 K (as can be clearly seen in Fig. 2). Given that the integrity of the crystal is more likely to remain closer to the original at the lowest temperature, an increase in the fraction of combination (and unknown) product suggests a higher barrier for the disproportionation reaction.

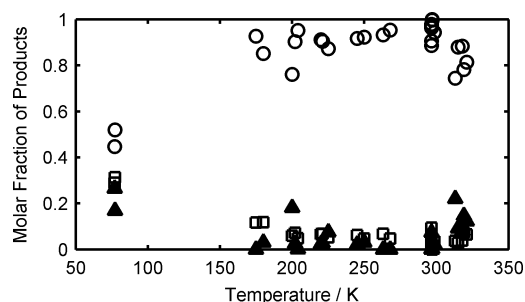


Fig. 2 Product distribution in the photolysis of the diazene in the solid state as a function of temperature. Circles, squares and triangles represent disproportionation, combination, and unknown products, respectively.

An Arrhenius plot for the ratio of disproportionation to combination products in Fig. 3 shows an increase from a low value of *ca.* 2 at 77 K to a maximum of 25–30 (between 170 to 320 K). Assuming the product ratio is determined by the first order rate constants of the corresponding reactions, the difference in activation energy between the two reactions is *ca.* $E_{a,\text{disp}} - E_{a,\text{comb}} = 2.1 \text{ kJ mol}^{-1}$. A linear regression of the data in Fig. 3 unveils the fact that A_{disp} is 55 times greater than A_{comb} , indicating the higher entropic requirement of the combination reaction ($\Delta S_{\text{disp}}^{\ddagger} - \Delta S_{\text{comb}}^{\ddagger} = 33 \text{ J K}^{-1} \text{ mol}^{-1}$).

In contrast to the relatively efficient diazene reaction, irradiation of crystalline 2,4-bis(biphenyl-4-yl)-2,4-dimethyl-pentan-3-one yielded only 50% product after 48 h. A rough comparison indicates that reaction in crystals of the diazene is at least about

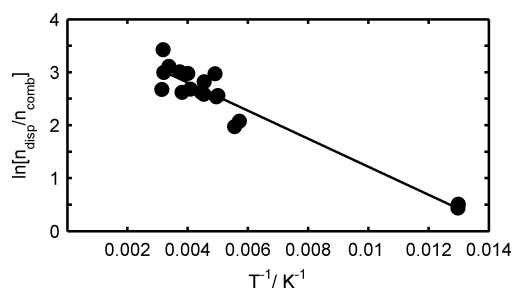


Fig. 3 Arrhenius plot of the ratio of disproportionation to combination products in the solid state photolysis of the diazene.

50 times more efficient than in crystals of the ketone. As in many previous examples of radical pairs derived from ketones, only the radical combination product biBME was detected.²⁷

Photochemistry in solution

Irradiation experiments in solution with the ketone and the diazene were carried out in cyclohexane at room temperature. The ketone yielded the combination product biBME in 78% yield, and the disproportionation products *i*-PB and *i*-PenB, in 11% yield each. From the photolysis of the diazene we detected the combination products biBME and TMPB in relative yields of 14 and 50%, respectively, and the disproportionation products *i*-PB and *i*-PenB in 8 and 28% yields, respectively. These values are included in Table 1 as the yield fraction. The more volatile products *i*-Bu, *i*-Buen, and TMBu were not observable under the conditions of our analysis (see below). Products arising from addition of a radical into the *ortho*-position of the aromatic ring of a BME[•] radical, often referred to as “semibenzenes”, play a minor role, as detected by NMR.^{28–30} They accounted for less than 5% of the

Table 1 Product distribution in the photolysis of the diazene and of the ketone in solution

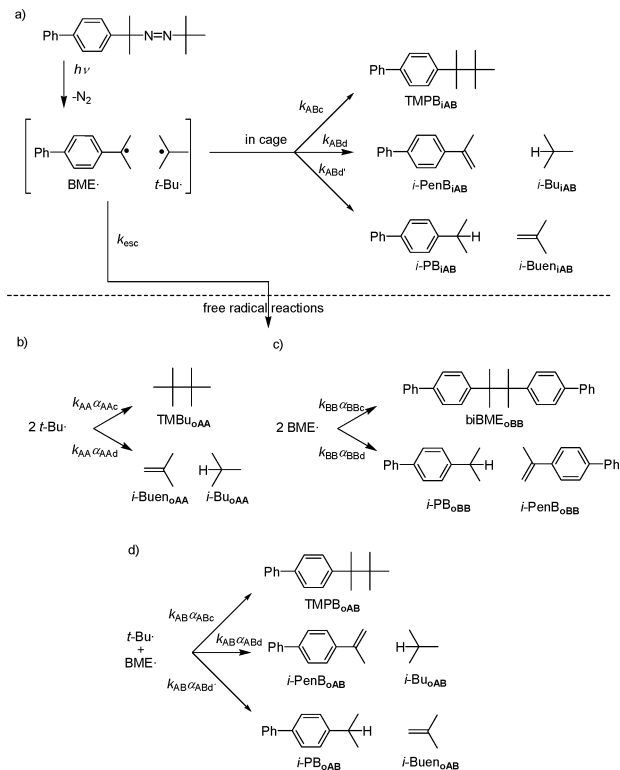
	Diazene 19.1%	Diazene 9.4%	Diazene 7.8%	Ketone 10–20% ^a
Measured yield fraction				
biBME	0.16	0.14	0.12	0.78
TMPB	0.49	0.51	0.49	—
<i>i</i> -PB	0.09	0.08	0.08	0.11
<i>i</i> -PenB	0.26	0.27	0.31	0.11
Calculated yield fraction				
biBME _{oBB}	0.16	0.14	0.12	—
TMPB _{iAB}	0.27	0.31	0.33	—
TMPB _{oAB}	0.22	0.20	0.16	—
<i>i</i> -PB _{iAB}	0.037	0.033	0.047	—
<i>i</i> -PB _{oAB}	0.031	0.022	0.022	—
<i>i</i> -PB _{oBB}	0.022	0.020	0.017	—
<i>i</i> -PenB _{iAB}	0.13	0.15	0.20	—
<i>i</i> -PenB _{oAB}	0.11	0.10	0.09	—
<i>i</i> -PenB _{oBB}	0.022	0.020	0.017	—
α_{ABc}	0.23	0.27	0.30	—
α_{ABd}	0.11	0.13	0.18	—
$\alpha_{ABd'}$	0.03	0.03	0.04	—
α_{BBc}	0.33	0.38	0.45	—
α_{BBd}	0.046	0.052	0.063	—
Cage Factor (f_{cage})	0.38	0.43	0.52	—

Percentages in the reactants column represent conversion of the starting material.^a Average of three experiments.

total products. This has also been observed in the photolysis of azocumene and many dibenzyl ketones. These products were not considered for the calculations described below.

The quantum efficiency for the disappearance of the diazene under steady state photolysis conditions is $\phi_{\text{diazene}} = 0.38 \pm 0.05$ for irradiation at 254 nm and $\phi_{\text{diazene}} = 0.50 \pm 0.05$ for irradiation at 365 nm (average of three determinations at each wavelength). This difference suggests that fast internal conversion from the $^1\pi,\pi^*$ to the ground state competes with internal conversion to the dissociative $^1n,\pi^*$ state in a *ca.* 1 : 4 ratio.

The products from the diazene are consistent with the detailed mechanism illustrated in Scheme 2. The photoinduced elimination of N_2 giving a singlet radical pair along with reactions within the solvent cage are illustrated in Scheme 2a. The reactions of the free radicals and their products are illustrated in Schemes 2b–2d. In the case of the ketone, photodissociation occurs in the triplet excited state so that geminate radicals are formed in the triplet state and are able to escape from the solvent cage to generate free radicals. For this reason, the products of the ketone arise exclusively from the BME' free radical reactions, as detailed in Scheme 2c.



Scheme 2 Subscripts 'i' and 'o' indicate that the product was formed either 'inside' the geminate cage or 'outside' of it. Subscripts A or B indicate the identity of the radicals reacting to form the product. $\alpha_{ABC} = k_{ABC} / (k_{ABC} + k_{ABd} + k_{ABd'} + k_{esc})$ and corresponding expressions are valid for the other α fractions.

To keep track of their origins, product names in Scheme 2 have been tagged with a subscript indicator to include their formation either 'in' the cage or 'out' of it, and whether they come from the *t*-Bu' (A) and/or the BME' (B) radicals encounters. For example, *i*-PenB_{oBB} indicates that 4-isopropenyl-biphenyl was formed out-of-cage (o) by reaction of two BME' free radicals (BB) (Scheme 2c), and TMBP_{iAB} is a product formed "in" the solvent cage (i) from

radicals A and B (AB) (Scheme 2a). As the latter product can form either *in-cage* or *out-of-cage*, the tag allows us to formally distinguish the source and scenery of its formation. Also indicated in the scheme are the rate constants (*k*) and fraction of the diffusive pairs (α) engaged in a particular reaction, tagged in the same manner as the corresponding products.

Products arising from a given disproportionation reactions form in equal amounts. It should be noticed in Schemes 2c and 2d that *i*-PB is formed in a stoichiometric amount as *i*-PenB when two BME' radicals encounter (the quantities named *i*-PB_{oBB} and *i*-PenB_{oBB} in Table 1 and Scheme 2c), and by one of the possible disproportionations of *t*-Bu' and BME' radicals (Scheme 2d). To obtain all the product fractions in the section marked as "calculated yield fraction" in Table 1 we take into account the conservation of mass for all compounds and we make the following three assumptions: (1) We consider that the total out of cage encounters of radicals of the type *t*-Bu' with *t*-Bu', *t*-Bu' with BME', and BME' with BME' are in proportion 1 : 2 : 1; we assume that such radical pairs react with equal total rates. (2) We assume that product distribution for in-cage (geminate) and diffusive encounters of *t*-Bu' and BME' radicals is the same; and (3) we consider that product distribution for the reaction of two BME' radicals in the same solvent and temperature is independent of the radical precursor, either it is the ketone or the diazene. All the stoichiometric equations used to calculate the product distributions in Scheme 2 are detailed in the electronic supporting information (ESI) section. ‡

The cage factor (f_{cage}) was calculated from the ratio of products from BME' radicals (B) originated inside the cage to the total amount of products originating from the same radical. This is equal to the sum of all products with the 'i' subscript over the sum of all products with 'i' or 'o' subscripts with biBME_{oBB} summed twice, as it was originated by two escaping BME' radicals. Cage factor values determined in this manner are equivalent to the normal cage effect, $CE = (AB - (AA + BB)) / (AA + AB + BB)$, where the amount of AA in our case is assumed to be equal to that of BB, as the AA products could not be quantified by the employed analytical methods. From the results in Table 1 an average value $f_{\text{cage}} = 44\%$ is found. In addition to the cage factor, we calculate that the ratio of combination to disproportionation is 1.6 for encounters of *t*-Bu' and BME' radicals from the diazene and 7.1 for two BME' radicals from the ketone. These values are obtained from the average ratio TMBP_{iAB} / (*i*-PB_{iAB} + *i*-PenB_{iAB}) for the diazene and from the ratio biBME_{oBB} / *i*-PenB_{oBB} for the ketone (Table 1). These values are compared to the results obtained from photolysis of the crystalline solids in Table 2. The ratio of combination to disproportionation in the reaction of pairs of

Table 2 Ratios of disproportionation and combination reactions in solution and in the crystalline state

	Diazene crystal	Diazene solution	Ketone crystal	Ketone solution
$\alpha_{BBc} / \alpha_{BBd}; [\text{biBME}_{\text{BB}} / i\text{-PenB}_{\text{BB}}]$	—	7.1 ^a	>33	7.1
$\alpha_{ABC} / (\alpha_{ABd} + \alpha_{ABd'})$	~0.06 ^b	1.6	—	—
$[\text{TMBP}_{\text{iAB}} / (i\text{-PenB}_{\text{iAB}} + i\text{-PB}_{\text{iAB}})]$	>20	4.1	—	—
$\alpha_{ABd} / \alpha_{ABd'}; [i\text{-PenB}_{\text{iAB}} / i\text{-PB}_{\text{iAB}}]$	>20	4.1	—	—

^a In the case of diazene in solution the reaction is exclusively out of the cage (*i*-PenB_{oBB} / biBME_{oBB}). ^b Average of values above 200 K.

B[•] radicals, the proportion of combination of A[•] and B[•] radicals to the sum of their disproportionation products, and the ratio of the different disproportionations between A[•] and B[•] to produce *i*-PenB or *i*-PB, are all shown in Table 2.

Discussion

The photoinduced denitrogenation of (1-biphenyl-4-yl-1-methyl-ethyl)-*tert*-butyldiazene and the photodecarbonylation of 2,4-bis(biphenyl-4-yl)-2,4-dimethyl-pentan-3-one proceed smoothly in solution and in the solid state. For reactions in crystals under quite similar conditions, the diazene reacted *ca.* 50 times faster than the ketone. This can be easily explained because N₂ loss takes place in the sub-picosecond timescale,⁶ whereas CO loss from the BME-CO[•] acyl radical is expected to take place in the nanosecond timescale.³¹ For reactions in solution, we analyzed the yield fraction of all the products arising from the diazene in order to calculate the cage factor, the selectivity of the geminate singlet radical pair, and the selectivity of radical pairs formed by free radical encounters. Based on literature results with analogous dicumylketones, we assumed that triplet radical pairs from the 2,4-bis(biphenyl-4-yl)-2,4-dimethyl-pentan-3-one completely escape the solvent cage showing a cage factor of zero.⁸

The two compounds photolyzed in this work allow us to compare the reaction pathways of two pairs of radicals (two BME[•] and a BME[•] and a *t*-Bu[•] radical pair) in solution and in the solid state. Additionally we are able to compare the relative weight of the disproportionation pathway of BME[•] reacting with itself, and with *t*-Bu[•] radical.

While radical-radical reactions in solution are determined primarily by the intrinsic reactivity of the corresponding radical pairs, reactions in crystals are strongly influenced by the structural constraints imposed by the reaction cavity, determined by the size and shape of the reactant. The data shown in Table 2 indicate that combination is more important than disproportionation when two BME[•] radicals react (first entry). A combination to disproportionation ratio of 7.1 represents the intrinsic reactivity of the BME[•] radicals. The same relation increases to >33 when the geminate radical pair is formed in crystals of the ketone. It is interesting that the combination to disproportionation ratio decreases to 1.6 for reactions of A and B radicals in solution, suggesting that combination may be more hindered when the *tert*-butyl radical is involved, and/or that the *t*-Bu[•] radical has a greater intrinsic reactivity towards hydrogen abstraction as compared to BME[•].^{29,32} These observations are in line with disproportionation being 5 to 7 times more probable than combination in the reaction of *t*-Bu[•] radicals in pentane or benzene.³³ Formation of the AB radical pair on the crystalline diazene photolysis resulted in a remarkable modification of its intrinsic solution reactivity. An enhancement in the yield of disproportionation in the crystalline diazene was accompanied by a much greater selectivity for hydrogen abstraction by the *tert*-butyl radical, detected as a high yield of *i*-PenB.

One may consider that the higher selectivity for combination in the crystalline ketone as compared to the higher yield of disproportionation in the crystalline diazene may be related to differences in the distances and orientations of the corresponding radicals. Assuming that distances in the ground state precursors available from single crystal X-ray analysis give a qualitative indication

of the corresponding values in the reactive intermediates, one finds that initial distances on combination trajectories are *ca.* 1 Å shorter for BB radical pairs in the ketone as compared to the AB pairs in the diazene. A distance of 2.72 Å for the two quaternary C atoms in the BME substituents of the ketone is increased to 3.68 Å between the quaternary C-atoms of the BME moiety and the *t*-Bu substituent in the diazene (Fig. 4). Having to reach a final C–C distance of *ca.* 1.54 Å in the final product, we speculate that starting radical-radical distances correspond to the steep descent portion of the bond-forming energy surface in the ketone and to the more shallow portion of a similar potential in the case of the diazene (Fig. 5). For a similar analysis for disproportionation trajectories one may consider the distance between the incipient radical centers (BME[•] for the ketone and *t*-Bu[•] for the diazene) and the closest hydrogen atom in a methyl group of the complementary radical fragment. While values of 2.89 and 3.94 Å are determined for the ketone and the diazene, respectively, one must recognize that rehybridization of the radical center, from sp³ to sp², and the possibility of rotation of the methyl groups make these values a rough approximation. It is interesting that ground state structures would suggest starting C–H distances of 2.89 Å in the case of ketone that are much shorter than the sum of the van der Waals radii (3.7 Å). The fact that combination is favored over disproportionation for the ketone may indicate that the radical pair is more advanced towards the bond-forming reaction. Geometry of the diazene suggests that disproportionation trajectories start at longer distances. For the diazene, disproportionation dominates because its transition state is entropically favored over that of the combination reaction (by 33 J K⁻¹ mol⁻¹), overcoming by this means its slightly higher activation energy barrier (2 kJ mol⁻¹, see Fig. 3).

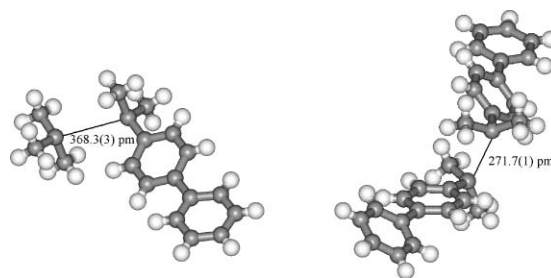


Fig. 4 Distance between C atoms bearing radical centers in the solid diazene (left), after N atoms removal, and in the solid ketone (right), after CO removal, derived from X-ray structures (Bruker SMART 1000 CCD-based).

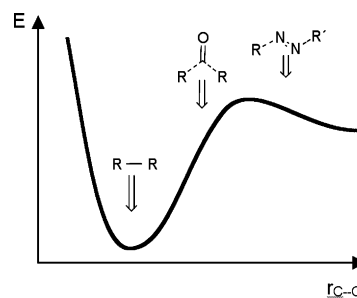


Fig. 5 Potential energy surface for bond formation for radical pairs formed in crystals from the ketone and the diazene. The arrows indicate the distance from which the reactive pair initiates the trajectory.

Our results include disproportionation to combination ratios analogous to those observed previously for other crystalline diazenes. The formation of 4-isopropenyl-biphenyl and isobutane (*i*-PenB and *i*-Bu) is favored over formation of 4-isopropyl-biphenyl and isobutene (*i*-PB and *i*-Buen). The former accounts for almost all of the disproportionation in the crystalline state (more than 95%), as only a small amount of *i*-PB is detected with NMR integration and HPLC analysis. This selectivity is lower in solution, but formation of *i*-PenB is still greater by a factor of 4. Based on quantum mechanical calculations, the more abundant disproportionation pair, *i*-PenB and *i*-Bu, is more stable by 7.64 kJ mol⁻¹. If entropic factors between the disproportionation reactions can be neglected, this energy difference predicts a ratio of 20 at 300 K for the amount of pairs of *i*-PenB and *i*-Bu to that of the pairs *i*-PB and *i*-Buen. This is in agreement with the results observed in the solid state. If we further take into account that the combination product is more stable than the *i*-PenB and *i*-Bu pair by 19.6 kJ mol⁻¹, one must conclude that the reaction occurs under kinetic control.

The photolysis of the diazene in the solid state shows that disproportionation accounts for more than 48% of the product mixture with up to 80% conversion values, and without crystal melting. Secondary photochemical reactions of the products can be excluded as an irradiation wavelength (355 nm) was chosen so that only the reactant would absorb light.

An Arrhenius plot of the disproportionation to combination ratio shows that disproportionation has an activation energy that is 2.1 kJ mol⁻¹ greater than the combination process, such that the amount of the combination product decreases as the temperature of the experiment rises. As this result is opposite to that reported by McBride with crystalline AIBN⁹ one must recognize the importance of specific molecular and packing effects on the reactivity of different crystalline diazenes.¹⁰

We can now compare the fate of the BME[•] radical in the photolysis of the diazene and of the ketone. In the former case, a singlet geminate radical pair is formed, while the dissociation of the ketone yields a triplet radical pair. Additionally, the radical centers are initially located at a greater distance after N₂ loss in the diazene photolysis than they are after CO loss in the ketone photolysis. This system, free of the entropic hindrance of the crystal reacts to yield the more stable combination products. The slower rate is due to the triplet nature of the diradical. On the other hand, singlet reactions of the radicals originated by the diazene react much faster and the H atom transfer probably overcomes the barrier of the greater distance between the radical centers by tunnelling, taking advantage of the entropic barrier that slows the combination down.

In conclusion, the increase in the fraction of disproportionation products in the diazene compared to the ketone, either in the crystal or in solution, is driven by the H-abstraction capability of the *t*-Bu[•] radical. The greater distance in the location of the radical centers after detachment of the small fragment (CO or N₂) in the diazene is responsible for the high increase in the disproportionation pathway in the solid state reactions.

The optimum and obvious comparison point for the reactivity of the different radical pairs in the solid state would have been the use of the azoalkane with two BME[•] radical substituents: bis(1-biphenyl-4-yl-1-methyl-ethyl) diazene. We failed to synthesize this product. Nevertheless, using the corresponding ketone, and by

geometrical considerations as well as by reasonable reaction comparisons, we were able to explain the difference in reactivity in the solid state and find a reference for the reactivity of BME[•] radicals in solution.

Singlet BME-*t*-Bu radical pairs generated by electronic excitation of the diazene in cyclohexane display a 44% cage factor, an adequate value to be an efficient radical source and a confinement probe at the same time. The measurement of the relative yields of the four biphenyl containing products allows the cage factor to be evaluated, even though disproportionation products can arise from both “in-cage” and “out-of-cage” reactions.

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