The Photochemical Reaction of 1,1-dicyano-3-phenylbut-1-ene.

Simultaneous Occurrence of π-methane and di-π-methane Rearrangements

Francisco A. da Silva\textsuperscript{a,b}, Aurelio B.B. Ferreira\textsuperscript{b,*}, and Miguel G. Neumann\textsuperscript{a,*}

\textsuperscript{a}Instituto de Química de São Carlos, Universidade de São Paulo, C.P. 780, 13560-970 São Carlos - SP, Brazil

\textsuperscript{b}Departamento de Química, Instituto de Ciências Exatas, Universidade Federal Rural do Rio de Janeiro, 23851-970 Itaguaí - RJ, Brazil

The direct photolysis of 1,1-dicyano-3-phenylbut-1-ene (3-MDCN) was investigated at room temperature in solvents of different polarities (hexane, dichloromethane and acetonitrile). Cyclopropanes arising from both the di-π-methane and π-methane (1,2-H migration) processes were obtained as photoproducts. The structures of the products were elucidated by \textsuperscript{1}H-NMR, GC/MS, IR and chromatography. Relative quantum yield determination and GC analysis of sequential irradiations gave evidence that: i) no secondary reactions occur, even at high conversions; ii) the di-π-methane rearrangement is significantly more affected by the solvent variation than the π-methane reaction. Photosensitization with acetophenone or acetone did not yield any observable products. The existence of the simultaneous mechanisms and the observed effects were considered as evidence of a possible differentiation between localized and delocalized excitation on the excited state surface.

Keywords: organic photochemistry, di-π-methane rearrangement, π-methane rearrangement, 1,2-hydrogen-photomigration

Introduction

The photochemical formation of cyclopropanes from π-methane systems (Scheme 1) is a well known and quite general reaction\textsuperscript{1-4}.

A special case that has been widely studied\textsuperscript{5-9} arises for compounds with an sp\textsuperscript{3}-carbon supporting two π-bonds. The accepted mechanism for these reactions is a di-π-methane rearrangement that involves both π-bonds and can be formulated as a $\pi^2 + \sigma^2 + \pi^2$ concerted process\textsuperscript{10} or as the sequential formation of 1,4- and 1,3-diradicals\textsuperscript{11} (Scheme 1).

Scheme 1.
2A). An alternative mechanism proposed earlier\textsuperscript{12} (Scheme 2B), involves only one of the $\pi$-bonds, with the cyclopropane being formed in a $\pi^2 + \sigma^2$ concerted process,\textsuperscript{13} or by cyclization of a 1,3-diradical formed after a 1,2-migration.

In the presence of a second homoconjugated $\pi$-bond the di-$\pi$-methane rearrangement usually predominates, as proved by Hixon\textsuperscript{14} and Zimmerman and Little\textsuperscript{15} (Scheme 3).

The formation of different cyclopropanes from the same starting compound by both mechanisms should provide a good opportunity for comparative studies, since the reactivity ratios could be obtained directly from the quantum yields or from the chemical yields at low conversions.

Therefore, we report here the results of the photolysis of 1,1-dicyano-3-phenylbut-1-ene, 3-MDCN, and 1,1-dicyano-3-methyl-3-phenylbut-1-ene, 3-DMDCN. The former is, to our knowledge, the first example of a compound whose photoreaction proceeds simultaneously by both pathways with comparative rates. 2-MDCN and its single di-$\pi$-methane product\textsuperscript{16} were used for chromatographic and spectroscopic comparisons, and as actinometer with an already determined quantum yield.

**Experimental**

**General methods**

Irradiations at 254 nm were performed in a Rayonet photoreactor (The Southern New England Ultraviolet Co.) with low-pressure mercury arc lamps (RPR2537). In general, 3 or 4 mL of the solution of 3-MDCN with concentrations between 4.25 and 11.8 mM were placed in quartz tubes and deoxygenated by flushing thoroughly with nitrogen. After irradiation for the required time, 1 mL of the solution of the chromatographic standard was added and the reaction mixture was analyzed by gas chromatography.

All chemicals and solvents (spectrophotometric or HPLC grade) were from Aldrich or Merck and used without further purification.

The reaction mixtures were analyzed by; Gas chromatography (Shimadzu GC-14B and Varian 3300) using 25 m OV-1 or PONA capillary columns and 1-dodecene as internal standard; UV-VIS spectroscopy (Hitachi U2000); FTIR spectroscopy (Bomem MB 102); GC/MS (HP5890 / HP5970) and $^1$H-NMR (Bruker AC200, shifts in ppm from TMS).

**Syntheses**

3-MDCN was synthesized by a Knovenagel condensation\textsuperscript{17}. A mixture of 4 mmoles of 2-phenylpropanal (hydratropaldehyde), 5 mmoles of malononitrile, 3 mmoles of ammonium acetate, and 40 drops of glacial acetic acid were dissolved in 40 mL of benzene and refluxed for 4 h. In order to increase the amount of recovered products, a Dean-Strak-type distillation head was used to separate, by azeotropy, the produced water. The final yield after extraction and distillation of the reaction mass was 67% (colourless oil, 146 °C/0.75 torr). $\nu_{\text{max}}$/cm$^{-1}$ 3090m, 2990m, 2240s, 1600s, 1500s, 1450s and 700s; $\delta$H (200 MHz, Me$_4$Si) 7.35 (6 H, m, H vinyl + 5 H arom), 4.13 (1 H, dq, $J_{11.6}$ and $J_{7.0}$, H benzyl) and 1.54 (3 H, d, $J_{7.0}$, CH$_3$); m/z 183 (M$^+$ + 1, 10%), 182 (M$^+$, 83), 181 (100), 167 (55), 154 (30) and 140 (88). The NMR data is similar to that found by Kruger\textsuperscript{et al.} for the same compound\textsuperscript{18}.

2-Methyl-2-phenylpropanal used as a precursor in the synthesis of 3-DMDCN was obtained by a Grignard reaction between methyl mandelate and CH$_3$I with pinacol formation (78%), followed by H$_2$SO$_4$/AcOH/I$_2$ treatment (yield ~60%), as described by Wolfe\textsuperscript{et al.} The aldehyde was converted to 3-DMDCN with 61% yield by a
Knovenagel procedure, as described above. (Colourless oil, 138-142 °C/0.6 torr). \( \nu_{\text{max}}/\text{cm}^{-1} \) 3050m, 2980m, 2250s, 1600s, 1500s, 1450s and 750s; \( \delta_{\text{H}} \) (200 MHz, Me$_4$Si) 7.30 (6 H, m, H$_{\text{vinyl}}$ + 5 H$_{\text{arom}}$) and 1.70 (6 H, s); m/z 197 (M$^{++}$+1, 9%), 196 (M$^{++}$, 62), 195 (47), 181 (95), 154 (100) and 127 (40).

**2-MDCN.** was synthesized using similar conditions$^{20}$. This compound was used as actinometer and for chromatographic and spectroscopic comparisons, as its photolysis rendered a single product. The quantum yield, previously determined$^{16}$, using both trans-cis isomerization of trans-1-phenylbut-2-ene and potassium ferrioxalate, is 0.018.

The cyclopropane \( \text{CP.1} \) (see Scheme 5) was synthesized thermally$^{21}$. In a flask with an outer jacket with boiling toluene, 7.5 mmole of \( \beta \)-methylstyrene and 15 mmole of malononitrile were mixed under agitation with the catalyst [CuCl$_2$ (8 mmoles) / Cu(AcO)$_2$ (8 mmoles) / LiCl (12 mmoles)] in 20 mL of N,N-dimethylformamide. After refluxing for 5 h with stirring the mixture was concentrated and extracted with petroleum ether. The final yield after drying and distillation was 31% of a yellow oil. \( \nu_{\text{max}}/\text{cm}^{-1} \) 3090m, 2940m, 2240s, 1500m, 1450m, 790m, 740s and 650m. \( \nu_{\text{max}}/\text{cm}^{-1} \) 3084m, 2935m, 2250s, 1228m, 740m and 650m. E-CP.1 m/z 183 (M$^{++}$+1, 10%), 182 (M$^{++}$, 70), 181 (100), 167 (26), 154 (30) and 140 (55). Z-CP.1 m/z 183 (M$^{++}$+1, 12%), 182 (M$^{++}$, 70), 181 (100), 167 (30), 154 (30) and 140 (53). E-CP.1 \( \delta_{\text{H}} \) (200 MHz, Me$_4$Si) 7.35 (5 H, m, H$_{\text{arom}}$), 2.75 (1 H, d, J 8.4, CH$_{\text{benzyl}}$), 2.25 (1H, dq, J 8.4 and 6.2, CH), 1.30 (3H, d, J 6.2, CH$_3$). Z-CP.1 \( \delta_{\text{H}} \) (200 MHz, Me$_4$Si) 7.35 (5 H, m, H$_{\text{arom}}$), 3.05 (1 H, d, J 5.4, CH$_{\text{benzyl}}$), 2.25 (1 H, dq, J 5.4 and 6.4, CH) and 1.20 (3 H, d, J 6.4, CH$_3$). The geometric isomers were identified taking into account the anisotropy effect of the phenyl group, the coupling constants and the similarity of the cleavage patterns in MS.

**Results**

**Photolysis of 3-MDCN**

In order to identify the reaction products a preparative photolysis was carried out. Thus, 1.6 mmole of the dicynoolefin 3-MDCN in hexane (100 mL) were degassed and irradiated for 5 h. A yellow oil was obtained after concentration of the reaction mixture in vacuum. The fraction recovered by bulb-to-bulb distillation showed three products by GC analysis (areas corresponding to 66, 10 and 19%, approximately), as well as the substrate (3%). Chromatographic and spectroscopic comparisons with CP.1 obtained by catalytic thermal synthesis$^{21}$ and CP.2, obtained by the of photolysis 2-MDCN$^{10}$, allowed their identification as E- and Z-CP.1 and CP.2. The spectroscopic data for CP.2 was \( \nu_{\text{max}}/\text{cm}^{-1} \) 3084m, 2935m, 2250s, 1228m, 740s and 650m; m/z 183 (M$^{++}$+1, 11%), 182 (M$^{++}$, 76), 181 (100), 167 (72), 154 (30) and 140 (63); \( \delta_{\text{H}} \) (200 MHz, Me$_4$Si) 7.35 (5 H, m, H$_{\text{arom}}$), 2.20 (1 H, d, J 6.0, H of CH$_2$), 1.80 (1 H, d, J 6.0, H of CH$_2$) and 1.65 (3 H, s, CH$_3$). Double irradiation experiments on the reaction mixture confirmed coupling between the ring protons in each cyclopropane (e.g., for CP.2, upon irradiation at 2.20\( \delta \) the doublet at 1.80\( \delta \) collapsed and vice-versa). The analysis of the products confirms the photoreaction reaction scheme (Scheme 5) leading to two cyclopropanes arising from the di-\( \pi \)-methane (CP.1) and \( \pi \)-methane (CP.2) rearrangements, respectively.

The absorption spectrum of 3-MDCN and its time evolution during photolysis are shown in Fig. 1. A blue-shift of the band around 230-220 nm during the photolysis, as well as the general decrease of the absorbance at wavelengths below 280 nm, suggests a bichromophoric interaction between the phenyl group and the double bond, which will be destroyed during the reaction.

It can be seen from Fig. 2, that the sum of the amounts of both cyclopropanes obtained during the photolysis is always equal to the consumption of 3-MDCN. This indicates a competition between the mechanisms leading to

**Figure 1.** Spectral changes of 3-MDCN in hexane (1.86 x 10$^{-4}$ M) when irradiated at 254 nm.
both photoproducts. Similar behavior can also be observed when the reaction is carried out in acetonitrile or dichloromethane. In addition, the ratio between both cyclopropanes also remains constant throughout the reaction, up to high conversions. This proves that there is no photochemical interconversion between the products CP.1 and CP.2, as expected from the low extinction coefficients of the cyclopropanes at the irradiation wavelength (i.e., at 254 nm, εCP.1 ≈ 5000, εCP.1 ≈ εCP.2 ≈ 200 M⁻¹ cm⁻¹).

**Solvent effect**

The photolysis of 3-MDCN was performed in three solvents with different polarity. The quantum yields for both cyclopropanes (i.e. both types of rearrangements) are shown in Table 1. The overall conversion is influenced by the solvent polarity due to the effect on the di-π-methane rearrangement. The formation of CP.1 always prevails over that of CP.2 (π-methane rearrangement), the latter practically not being affected by the change of solvent.

**Photolysis of 3-DMDCN**

To compare with the results obtained for 3-MDCN, a hexane solution of 3-DMDCN (2.57 mmol/100mL) was photolyzed for 6 h. Only one product was observed, corresponding to the di-π-methane rearrangement. It crystallized in the reaction solvent (white crystals, m.p. = 62-65 °C) with a yield of 41% and was identified as CP.3. The corresponding spectroscopic data are: νmax/cm⁻¹ 3040m, 2960m, 2240s, 1400s, 760s and 700s; m/z 197 (M⁺, CH benzyl), 1.73 (3 H, s, CH₃) and 1.32 (3 H, s, CH₃).

No products were observed when attempting to sensitize the reaction of 3-MDCN and 3-DMDCN in hexane with acetonitrile (Eₜ = 74 kcal/mol) or acetone (Eₜ = 78 kcal/mol).

**Discussion**

The absorption spectrum of 3-MDCN suggests a bichromophoric interaction as the extinction coefficients in the 230 and 270 nm regions (ε230 = 3610 and ε270 = 10000 M⁻¹ cm⁻¹) are larger than those corresponding to the separate chromophores (ε261max = 295 M⁻¹ cm⁻¹ for toluene). The same behaviour has been observed also for 2-MDCN. The increase of the extinction coefficient for similar compounds was assumed to be due to the excitation to a delocalized state (aromatic π + double bond π*)[2224]. In this interaction the phenyl group acts as the donor and the double bond as the acceptor, giving rise to a charge transfer complex in the vertical excited state. Assuming that the 1,2-migration of H results from electronic excitation on the double bond, the observation of products resulting from both mechanisms from the same compound, suggests the excitation to a delocalized orbital.

The absorption peaks in the short wavelength region of the spectrum of 3-MDCN can be ascribed to the transitions to localized and delocalized states, both having singlet character. Those states correspond to potential energy surfaces that lead to different photoproducts. On the lower energy surface, corresponding to the delocalized excited state, excitation leads to a charge-transfer complex (CTC), which will take to the di-π-methane rearrangement. The increase of solvent polarity will stabilize this complex, decreasing the quantum yield of CP.1, ΦCP.1. The 1-2 H photomigration (or π-methane rearrangement) originates from the localized excited surface. A possible potential
energy scheme is shown in Fig. 3. The small effect of the solvent polarity on $\Phi_{CP.2}$ seems to indicate that the excited state surface leading to the 1,2-photomigration of H has a more accentuated radical character. The pathway on this surface should not be affected by the motions leading to the surface corresponding to the di-π-methane rearrangement (”touching” motion between both π moieties$^{25}$).

On the surface leading to the CP.1 formation, the charge transfer complex in the excited state is stabilized by polar solvents, decreasing the formation rate of this cyclopropane. This decrease in the efficiency of di-π-methane rearrangement ($\Phi_{CP.1}$) with increasing solvent polarity has already been observed before$^{16,20}$. It was considered an evidence for the competition between the deactivation of the excited singlet state by reversible electron transfer from the phenyl group to the dicyanovinyl moiety, and the formation of a 1,4-diradical leading to homolytic ring-opening and reclosure on the di-π-methane pathway. Both processes originate from the same intramolecular motion from the vertical excited state (“touching”). This deactivation process by electron transfer between two chromophores was also proposed for di-π-methane rearrangements in the triplet state$^{26}$.

Previous studies on similar systems proved that both mechanisms (π-methane$^{4,14}$ and di-π-methane$^{22,24}$) originate from singlet excited states. For the structurally related compound in which one of the CN groups is replaced by an ester, the sensitization with acetophenone leads to isomerization around the double bond, with no formation of cyclopropanes. The latter were only observed upon direct photolysis with 254 nm light. From these results it can be assumed that triplet states are not involved in the photo-reactions of 3-MDCN and 3-DMDCN, which should proceed via a singlet excited state.

In general, from data found in the literature (Scheme 3) it can be seen that the diπ-methane rearrangement is much more efficient than the π-methane reaction. As expected, the photomigration is easier for hydrogen than for methyl group, as found when comparing the photochemistry of 3-MDCN with that of 3-DMDCN, where only the di-π-methane process occurs, with the same efficiency as for 3-MDCN ($\Phi_{CP.3} = 0.054$). The photochemistry of 2-MDCN should show the same products as 3-MDCN, wouldn’t it be by the inhibition of the 1,2 photomigration by substitution on the end carbon of the migration, due probably to steric and electronic effects$^4$. Thus, 3-MDCN seems to be the only compound for which both mechanisms occur simultaneously with comparable efficiency.

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**References**


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