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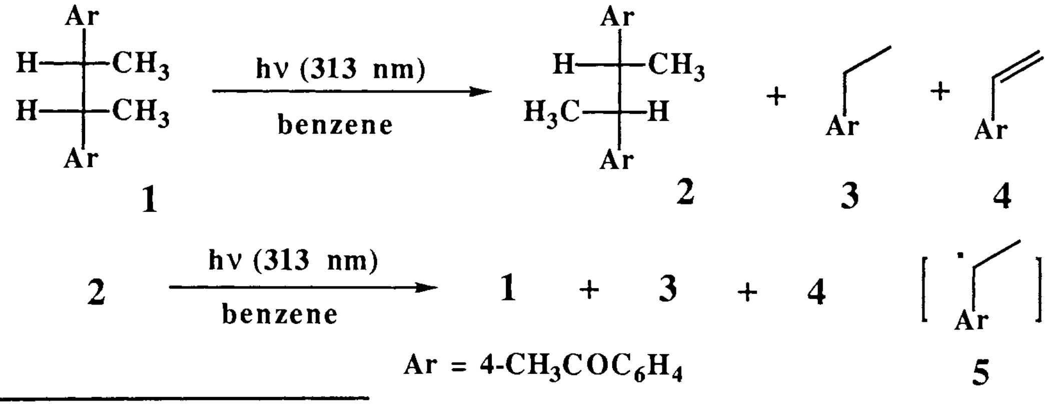
Photocleavage of C-C Single Bond of 1,2-Bis(4-acetylphenyl)ethane Derivatives

Nobuyuki ICHINOSE,† Kazuhiko MIZUNO,* and Yoshio OTSUJI*
Department of Applied Chemistry, College of Engineering,
University of Osaka Prefecture, Sakai, Osaka 593

1,2-Bis(4-acetylphenyl)ethanes undergo a novel meso-dl photoisomerization via the C_1-C_2 σ bond cleavage from their excited triplets. Comparison between acyclic and cyclic derivatives suggests that the energy barrier for the conformational change leading to the transition state with maximum σ-π orbital interaction, as well as the molecular strain estimated by MM2 calculations, plays an important role in determining the photochemical reactivity of the compounds.

Molecular strain often plays an important role in determining reactivity of chemical reactions. Rüchardt and Beckhaus have studied the thermal cleavage of various hydrocarbons and demonstrated that their reactivity can be explained in terms of strain energy within the molecules.[1] We now report a novel photochemical C-C bond cleavage reaction of acyclic and cyclic alkanes having two 4-acetylphenyl substituents at vicinal positions. We also demonstrate on the basis of MM2 force field calculations that a conformational factor of the molecules, as well as molecular strain, may play an important part in determining the reactivity of this photoreaction.

When a degassed benzene solution of meso-2,3-bis(4-acetylphenyl)butane (**1**, 4×10^{-3} mol dm^{-3}) was irradiated with UV light at 313 nm, this compound was isomerized gradually to the dl-isomer **2**, accompanying the formation of small amounts (< 5%) of 1-acetyl-4-ethylbenzene (**3**) and 1-acetyl-4-vinylbenzene (**4**). Irradiation of **2** in a similar manner also gave a mixture of **1** - **4**.[2,3] The quantum yield for the conversion of **1**→**2** was 0.02 and that for the conversion of **2**→**1** was 0.06 at room temperature (Fig.1).



Ar = 4-$CH_3COC_6H_4$

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† Present address: Microphotoconversion Project, ERATO, Research and Development Corporation of Japan, 1280 Kami-izumi, Sodegaura, Chiba 299-02.

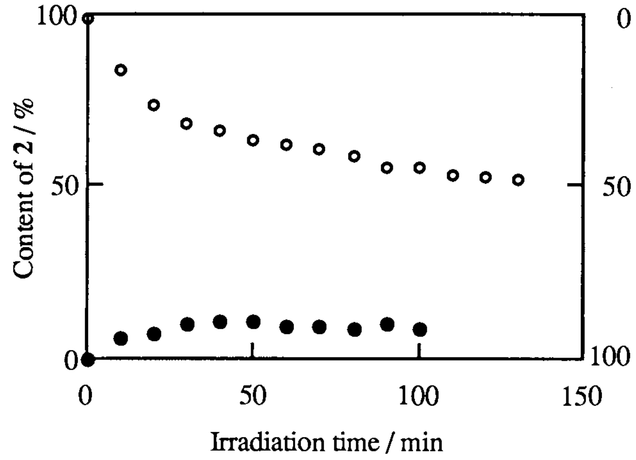


Fig. 1. Plots of amounts of **1** and **2** (%) vs. irradiation time (min): [**1**] = [**2**] = 4 x 10^{-3} mol dm^{-3} in benzene.
● : Photoisomerization of **1** to **2**,
○ : Photoisomerization of **2** to **1**.

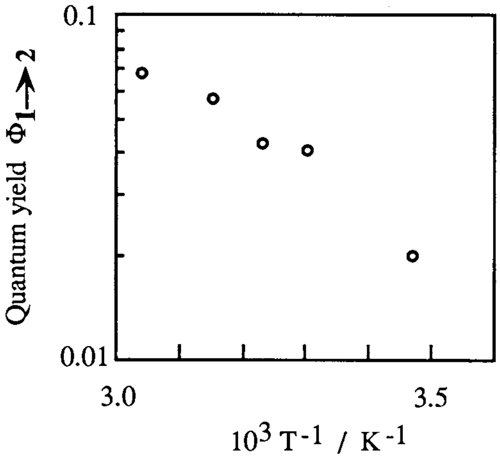
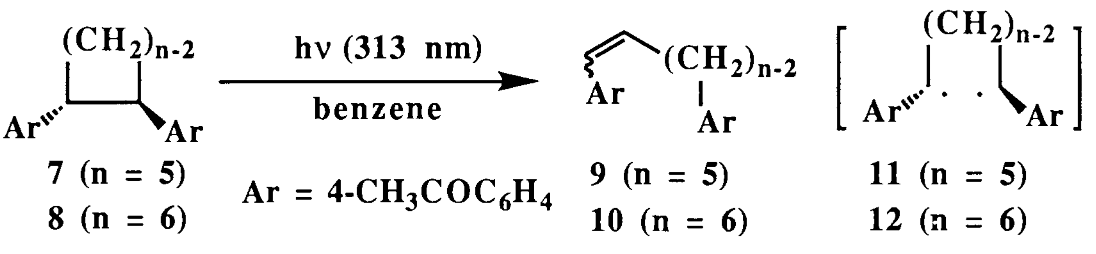
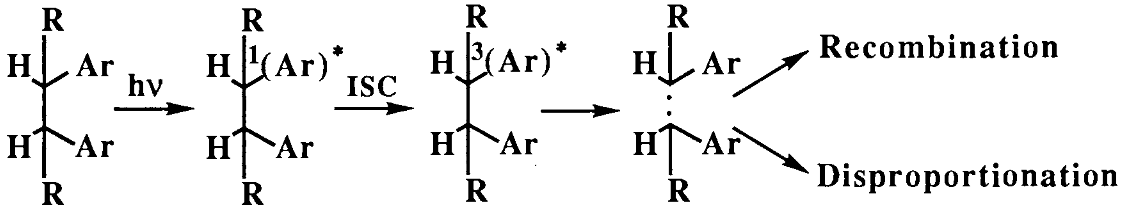


Fig. 2. A log plot of the quantum yields for the photoisomerization of **1** to **2** vs. T^{-1}.

The photoisomerization of **1** was thermally enhanced (Fig. 2). The quantum yield for the conversion of **1**→**2** was increased by a factor 3.4 when the temperature was elevated from 15 °C to 55 °C. Compounds **1** and **2** were thermally stable and did not undergo a pyrolytic reaction up to 300 °C. The photoreactions of **1** and **2** were completely quenched by adding 2-methyl-1,3-butadiene (0.1 mol dm^{-3}) or molecular dioxygen (0.01 mol dm^{-3}). In the case of the photoreaction of **1**, the addition of ethanethiol depressed the formation of **2**-**4**, but instead led to the formation of alcohols that were produced by reduction of the acetyl groups. These results suggest that the photoreactions of **1** and **2** proceed via their acetophenone-type excited triplets. They also imply that the C-C single bond cleavage occurs from these triplets to give 1-(4-acetylphenyl)ethan-1-yl (**5**) which converts into the isomerization product by recombination and also **3** and **4** by disproportionation (Scheme 1). However, irradiation of 1-(4-acetylphenyl)-2-phenylethane (**6**) under the similar conditions did not afford any photocleavage products such as 1,2-diphenylethane and 1,2-bis(4-acetylphenyl)ethane even at 80 °C, although the photoreaction in the presence of ethanethiol gave the corresponding alcohol. This indicates that the excited triplet of **6** undergoes hydrogen abstraction from ethanethiol, but does not undergo C-C bond cleavage.

The photoreaction of trans-1,2-bis(4-acetylphenyl)cyclopentane (**7**) and trans-1,2-bis(4-acetylphenyl)-cyclohexane (**8**) gave, respectively, small amounts (3-5%) of 1,5-bis(4-acetylphenyl)-1-pentene (**9**) and 1,6-





R, R = CH_3, CH_3 ; -$(CH_2)_{n-2}$- (n = 5, 6) Ar = 4-$CH_3COC_6H_4$

Scheme 1.

bis(4-acetylphenyl)-1-hexene (**10**) as a mixture of E- and Z-isomers.[2] Quantum yields for the formation of **9** and **10** were less than 0.01. These products are likely to be produced from 1,5- and 1,6-biradicals, **11** and **12**, that are formed by the C_1-C_2 bond cleavage of **7** and **8**. The formation of **9** and **10** was also completely quenched by adding 2-methyl-1,3-butadiene (0.1 mol dm^{-3}) or molecular dioxygen. This also suggests that the photocleavage reaction of **7** and **8** proceeds via their excited triplets.

The photochemical process shown in Scheme 1 is supposed to be exothermic on the basis of the data that the energy of acetophenone-type triplet is 302 kJ mol^{-1},[4] the C-C bond energy is 356 kJ mol^{-1},[5] and the stabilization energy of two benzylic radicals is 52 kJ mol^{-1} x 2 = 104 kJ mol^{-1} [6,7]: The estimated value for the heat of the photocleavage reaction from these values is -50 kJ mol^{-1} (356 - 302 - 104 = -50). However, the thermal enhancement of the photoreaction of **1** suggests that some thermal activation is required for the C-C bond cleavage from its excited triplet. Previously, we reported that excited triplets of trans- and cis-1,2-bis(4-acetylphenyl)cyclopropanes convert spontaneously into the corresponding 1,3-biradicals without being quenched by 2-methyl-1,3-butadiene.[6] The excited triplet of 1,2-bis(4-acetylphenyl)cyclobutane was also cleaved rapidly to give the 1,4-biradical without being quenched by 2-methyl-1,3-butadiene.[8] Apparently, in these molecules a large ring strain within 3- and 4-membered rings make their triplets highly reactive. The ring strain energy has been estimated to be 113 kJ mol^{-1} for both cyclopropane and cyclobutane.[9]

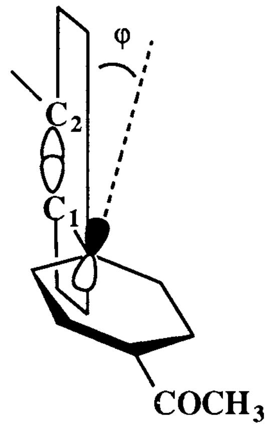


Fig. 3. Definition of dihedral angle φ between interacting σ-π orbitals (see text).

Table 1. Total Strain Energies and Dihedral Angles between σ-π Orbitals Obtained by MM2(85) Force Field Optimization

Compd	Total strain energy / kJ mol^{-1}	$\varphi^{a)}$ / deg
1	46.9	18.8
2	57.0	1.7
6	33.5	0.0
8	57.8	22.6

a) Dihedral angles: see Fig. 3.

In order to gain insight into factors determining the photochemical reactivity, MM2 (85) force field calculations were carried out for **1**, **2**, **6**, and **8**.[10] The results are given in Table 1. Strain energies of all the compounds are not much different from each other and also not so large, although that of **6** is a little smaller than those of other compounds. However, the dihedral angle between the plane of their 4-acetylphenyl ring and their C_1-C_2 σ bond varies widely (Fig. 3). The 4-acetylphenyl ring lies perpendicular to the C_1-C_2 bond axis in **2** and **6**, but not in **1** and **8**. This indicates that a σ-π interaction between the σ-orbital of C_1-C_2 bond and the π-orbital of 4-acetylphenyl ring is larger in **2** and **6**.

It is reasonable to suppose that the photochemical C-C bond cleavage is caused by a conversion of the electronic state from the $^3(n,\pi^*)$ state of the acetyl group of 4-acetylphenyl ring into the the anti-bonding $^3(\sigma,\sigma^*)$ state of the C_1-C_2 σ bond. This conversion is apparently much more efficient for **2** and also for **1** than for **7** and **8**, because the σ-π (and/of σ^*-π^*) orbital interaction is large in the former compounds. In the transition state of the photocleavage reaction, the molecules will adopt a more energetically favorable conformation in which the overlap of σ and π (and/of σ^* and π^*) orbitals become maximal. The larger σ-π (and/of σ^*-π^*) interaction in **1** and **2** particularly in **2**, results in the higher photochemical reactivity of these compounds, compared with that of **7** and **8**. The less reactivity of **6** may be ascribed to a less stability of the resulting radical, in addition to a smaller strain energy of the reactant molecule. Furthermore, the MM2-calculated optimized structures and the CPK models indicate that the internal rotation of the 4-acetylphenyl rings of **7** and **8** must be highly restricted because of their cyclic structures. On the other hand, the energy barriers for the internal rotation will be negligibly small for and **2**. These enegy barriers must be overcome for the efficient photocleavage reaction to occur in **7** and **8**. In conclusion, the energy barrier for the conformational change leading to the efficient σ-π (and/of σ^*-π^*) interaction, as well as the molecular strain and the stability of the resulting radicals, plays an important role for the photocleavage reaction of C-C single bonds in the title compounds.

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