

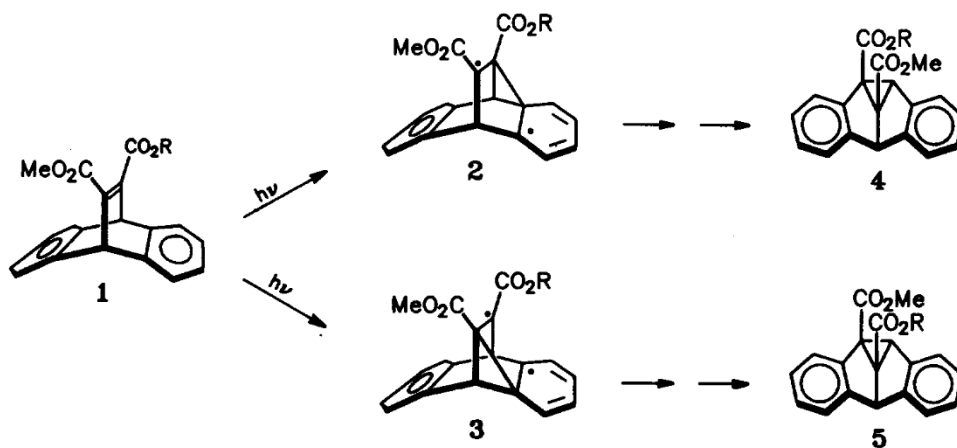
INTERMOLECULAR STERIC EFFECTS ON UNIMOLECULAR REARRANGEMENTS IN CRYSTALLINE MEDIA

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Abstract. As a result of steric interactions between the reacting molecule and its nearest neighbors in the crystal lattice, the regioselectivity of the di- π -methane photorearrangement of dibenzobarrelene diesters is greatly altered in the solid state compared to isotropic liquid media.

For unimolecular chemical processes, the essentially random steric interactions between reactant solutes and isotropic liquid solvents generally play no role in determining product structure. In the crystalline environment, however, where the constituent molecules are packed in an ordered arrangement within van der Waals distances of one another, it is virtually inevitable that chemical reaction of one of their number will involve steric contact with the surrounding lattice. In this communication we report how such steric effects appear to alter dramatically the regioselectivity of the di- π -methane photorearrangement of dibenzobarrelene diesters.

The compounds studied were the dibenzobarrelene diesters **1a** - **1d** (Scheme) prepared by conventional methods from the readily available dimethyl analogue.¹ Preparative scale irradiations in benzene using a 450 W Hanovia lamp fitted with a Pyrex filter gave mixtures of the dibenzosemibullvalene derivatives **4** and **5**.² Compounds **4b** (mp 139-141°) and **5b** (mp 110-112°) were isolated and their structures established by X-ray crystallography.³ ¹H NMR



(a) R=Et; (b) R=iPr; (c) R=(\pm)sBu; (d) R=tBu

spectroscopy of these regioisomers revealed that the methyl resonance of **4b** appeared at a higher field (δ 3.70) than that of **5b** (δ 3.86), and this fact was used in establishing the regiochemistry of the photoproducts from diesters **1a**, **1c** and **1d**.

The differences observed in irradiating diesters **1a** - **1d** in the crystalline state and solution (benzene) are summarized in the Table. Photolyses were carried out to low conversions (< 30%) at room temperature using either a 450 W medium pressure mercury lamp (Pyrex filter) or a nitrogen laser (337 nm). Crystal irradiations were conducted on both single crystal and polycrystalline samples with no variation in the results; there was no discernable crystal melting.

Solution vs Crystal Phase Di- π -methane Regioselectivity for Unsymmetrical Diesters

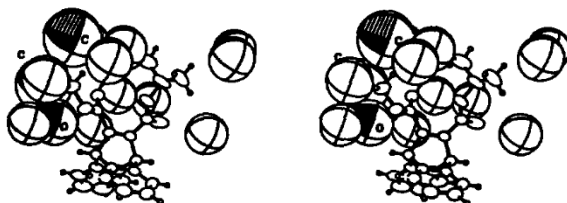
Diester	mp	4:5 Ratio	
		Benzene	Crystal
1a	104-106°	53:47	45:55
1b	124-125°	55:45	93:7
1c	95-97°	60:40	99:1
1d	128-129°	60:40	15:85

The results demonstrate a striking variation in reaction regioselectivity between the crystalline and solution media. Only the methyl-ethyl diester **1a** gave photoproduct ratios that did not vary much with change of phase. Interestingly, while there was a slight (but uniform) regiochemical preference in solution for the smaller ester group to occupy the less hindered apical position of the semibullvalene ring system, such was not the case in the solid state, where the 4:5 ratio ranged from 99:1 (compound **1c**) to 15:85 (compound **1d**).

There are at least two possible explanations for the phase-dependent photoproduct ratio differences. The first is the possibility that the crystal lattice may enforce different degrees of conjugation between the non-equivalent ester groups and the double bond between them. This would tend to favor initial benzo-vinyl bridging at the vinyl carbon atom that is less conjugated with its attached ester group (reaction at the site with greater excited state odd-electron character; formation of the more highly resonance stabilized biradical intermediate). Schaffner, et al.⁴ have reported a di- π -methane reaction where such an effect appears to be operative in a frozen glass at 77K. This explanation is not consistent, however, with the crystal structure for diester **1b**.⁵ Although the two ester groups of **1b** do overlap to slightly different extents with the central double bond (45° vs 37° deviation from coplanarity), reaction occurs at the vinylic center that is more conjugated (37°) to the CO₂iPr ester

substituent. Similar results were observed in the case of the isopropyl-(\pm)sec-butyl diester,⁶ and we thus tentatively conclude that excited state electron distribution and biradical stabilization differences brought about by conformational rigidity in the solid state are not controlling the reaction regioselectivities of diesters 1a - 1d.

A second explanation for the observed solid state regioselectivities involves the possibility that steric effects between the reacting molecule and its lattice neighbors may be the controlling factor. It is evident from molecular models that benzo-vinyl bridging involves substantial atomic motions, particularly of the ester groups, and perhaps the regioselectivities can be related to differences in the free lattice space around each of the non-equivalent ester groups. The packing differences around the methyl and isopropyl ester groups of compound 1b are depicted in the figure below.



Stereodiagram showing van der Waals radii of contact atoms at $d < 3 \text{ \AA}$ in molecules surrounding 1b. Carbon and oxygen atoms are labeled; the remainder are hydrogen atoms.

Qualitatively, it is apparent that the methyl ester group is more tightly surrounded by neighboring atoms than is the isopropyl ester group. This is consistent with the experimental results, which require initial bonding at the vinyl carbon atom bearing the isopropyl ester group. Computer simulation of the initial stages of benzo-vinyl bridging supports these conclusions. The Lennard-Jones non-bonded repulsion energies⁷ resulting from slight displacements of the CO_2iPr group in either direction are significantly less than those involved in moving the CO_2Me group.

An important point that emerges from the work described in this communication is that steric effects in the solid state are not as regular as they tend to be in solution. In solution, if a steric effect can be attributed to a substituent of moderate size, then increasing the bulk of the substituent usually brings about a similar but larger steric effect and vice versa. In the solid state, however, exchanging one substituent for another often leads to a completely different packing arrangement and steric environment. This can result, as we have seen for diesters 1a - 1d, in very different chemical behavior for closely related compounds.⁸

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2. The first example of this reaction was reported in solution for the corresponding dimethyl diester by E. Ciganek, J. Am. Chem. Soc., **88**, 2882 (1966).
3. Compound **4b**: $P2_{1/a}$, $R = 0.046$; Compound **5b**: $P2_{1/n}$, $R = 0.051$. Full details will be published separately.
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8. For related studies on crystal lattice steric effects in unimolecular chemical processes, see S. Ariel, S. Askari, S.V. Evans, C. Hwang, J. Jay, J.R. Scheffer, J. Trotter, L. Walsh and Y-F. Wong, Tetrahedron, **43**, 1253 (1987).

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