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STEREOSELECTIVITY REVERSAL OF A PHOTOCHEMICAL REACTION IN THE SOLID STATE

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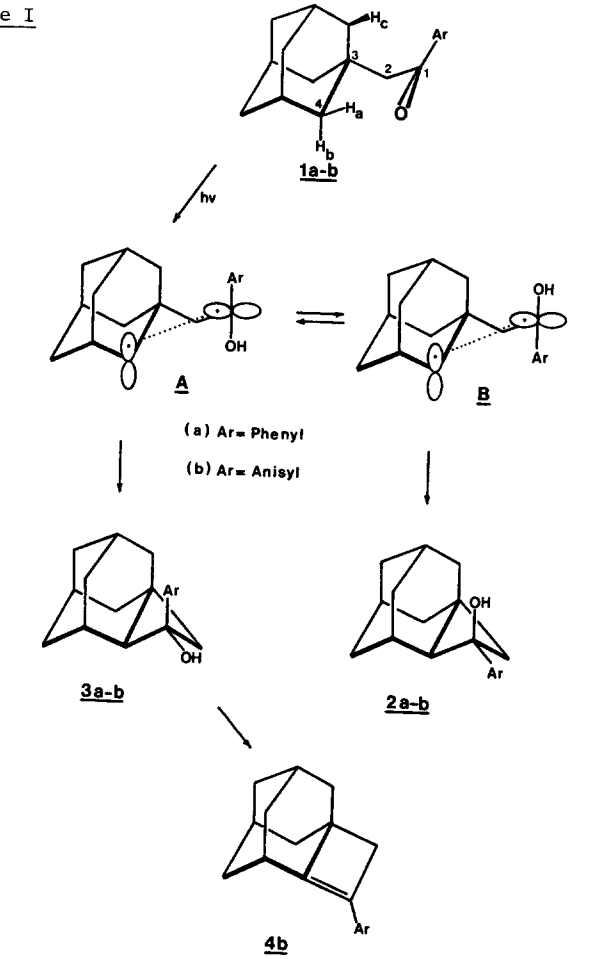
Abstract. The stereoselectivity of Norrish type II cyclobutanol formation resulting from photolysis of α-adamantyl-p-methoxyacetophenone is altered in favor of the more hindered cis isomer as the reaction medium is changed from isotropic liquid phases (benzene or acetonitrile) to the pure crystal. Based on the reactant X-ray crystal structure, it is suggested that the intermediate 1,4-biradical in the solid state is born in, and restricted to, a conformation which is ideal for direct closure to the more hindered product. In the relatively unrestricted solution environment, however, conformational isomerism of the biradical is faster than closure, thus leading to a predominance of the less hindered trans cyclobutanol.

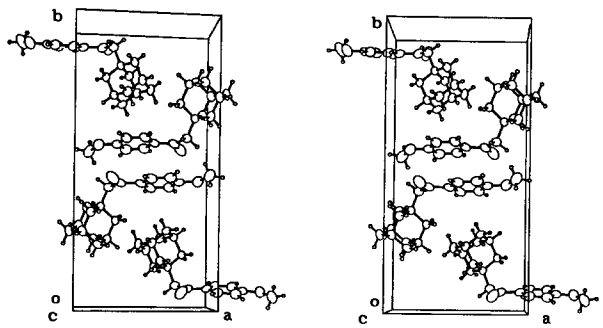
Dedicated to Professor Harry H. Wasserman on the occasion of his 65th birthday.

Of the several ways in which the organic crystalline phase can alter chemical reactivity compared to isotropic liquid media, one of the most intriguing involves its effect on the behavior of biradical intermediates. Previous studies from our laboratory have shown that the competition between 1,4-biradical cleavage and closure in the Norrish type II reaction is shifted strongly in favor of cleavage, the less motion process, by solid state immobilization.[1] Similar conclusions have been reached from studies of the Norrish type II reaction in other organized media such clathrate inclusion complexes,[2] zeolites[3] and liquid crystals.[4] In this communication we report that, in addition, the stereoselectivity of biradical closure (cyclobutanol formation) can be altered significantly in favor of the less motion pathway by the solid state medium, even though this pathway gives the more sterically hindered product.

The compound studied was α-adamantyl-p-methoxyacetophenone (1b, Scheme I), mp 80-81 °C, prepared by Friedel-Crafts acylation of anisole with adamantyl acetyl chloride. The choice of compound 1b was based on the work of Lewis, Johnson and Kory[5] who showed that photolysis of α-adamantylacetophenone (1a) in solution ($\Phi_{benzene}$ = 0.04) affords exclusively the cyclobutanols 2a and 3a (ratio 1.3 in benzene). We find that ketone 1b behaves analogously, affording upon irradiation with the output from a nitrogen laser (337 nm), the less hindered cyclobutanol 2b and the more hindered cyclobutanol 3b in a ratio of 2.6 in benzene and 2.0 in acetonitrile.[6] The quantum yields for ketone 1b, measured at 313 nm using valerophenone actinometry, were 0.08 in benzene and 0.12 in moist acetonitrile. Photoproduct 2b was separated by silica gel column chromatography and its structure assigned unambiguously by conventional spectroscopic methods. Cyclobutanol 3b was found to undergo facile dehydration to the cyclobutene derivative 4b (mp 110-112 °C) upon attempted chromatography. The identity of the dehydration product as 4b rather than the alternative regioisomer was established by proton and ^{13}C NMR spectroscopy, which indicated the presence of a molecular plane of symmetry.[7]

Scheme I





Stereodiagram of the crystal packing for α-adamantyl-p-methoxyacetophenone showing the parallel arrangement of neighboring aromatic rings. The interplanar distance is 3.62 Å.

In contrast to the solution results, laser irradiation of crystalline samples of ketone 1b afforded the more hindered cyclobutanol isomer 3b as the major product, the 2b/3b ratio being 0.5. This represents a complete reversal of stereoselectivity in the solid state. To probe the reasons for this dramatic change, we determined the X-ray crystal and molecular structure of ketone 1b. The results ($P2_1/n$, R = 0.051) show that compound 1b adopts a conformation (Scheme I) in which the most accessible γ-hydrogen atom, H_a, is that which forms a chairlike six atom arrangement with the abstracting carbonyl oxygen atom and the intervening carbon atoms. This stands in contrast to our previous studies which showed that a boatlike abstraction geometry is preferred for the Norrish type II reaction of α-cyclohexylacetophenones in the solid state.[1] It also differs from the conformation assumed by Gagosian, Dalton and Turro for the type II photoreaction of the closely related α-adamantylacetone.[8] The carbonyl oxygen to H_a distance for ketone 1b is 2.66 Å. This distance is consistent with our suggestion[9] that the approximate upper limit for hydrogen atom abstraction is the sum of the van der Waals radii of the atoms involved, 2.72 Å in the case of hydrogen and oxygen.[10] The oxygen to H_b distance, at 2.96 Å, is well above this limit, and the only other sterically accessible γ-hydrogen atom (H_c) also lies outside the limit (3.17 Å). The angle τ, by which the hydrogen atom H_a lies outside the mean plane of the carbonyl group, is 59.4° for ketone 1b. This value corroborates our previous conclusion[1] that coplanar hydrogen atom abstraction is not a prerequisite for the success of the Norrish type II reaction.

If we make the reasonable assumption that the intermediate 1,4-biradical has the same basic conformation as its ketonic precursor, a plausible explanation for the cyclobutanol ratios emerges. The X-ray data show that the O(1)-C(1)-C(2)-C(3) dihedral angle for ketone 1b is 83.3°. This means that the 1,4-biradical resulting from abstraction of hydrogen atom H_a will have essentially the 90,0 geometry shown in Scheme I (conformation A). Direct closure of this biradical leads to the more hindered cyclobutanol 3b. Formation of the less hindered cyclobutanol 2b, however, requires prior isomerization of conformer A by rotation about either the C(1)-C(2) or C(2)-C(3) bonds. One such process consists of a 180° rotation of the aryl group around the C(1)-C(2) bond. This leads to conformer B (Scheme I), which in turn closes to form 2b. Therefore, the predominance of cyclobutanol 3b in the solid state reflects the fact that its biradical precursor is born in a conformation ideally suited for its formation, whereas production of stereoisomer 2b requires a conformational isomerization which is retarded by the crystal lattice medium.[11] The packing diagram (Scheme I) indicates that this is the case. Nearest lattice neighbors have parallel aromatic rings which would clash violently upon attempted C(1)-C(2) bond rotation.[12] However, these steric interactions are absent in solution, and if, as seems likely, these same conformers are present in solution, the predominance of photoproduct 2b in this medium can be explained either by a preference for conformer B (less hindered) over conformer A (more hindered) or a faster rate of cyclization of B or both.

It is interesting to compare our cyclobutanol stereoselectivity results with those obtained in other organized media. Both Hrovat, et. al.[4] (photolysis of 10-nonadecanone in the smectic liquid crystalline phase of n-butyl stearate) and Casal, et. al.[2b] (photolysis of the crystalline urea inclusion complex of 5-nonanone) found that the proportion of the less hindered (trans) cyclobutanol stereoisomer increased in proceeding from the less ordered to the more ordered phase. On the other hand, Goswami, et. al.[2a] (Norrish type II reaction of the crystalline complexes formed

between aralkyl ketones and Dianin's compound) as well as Ariel, et. al.[1] (irradiation of type II ketones in the pure crystalline state) noted little difference in cyclobutanol stereoselectivity compared to the solution results. Clearly, not all organized media exert the same effect.

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11. The preference for more hindered (cis) cyclobutanol formation from the singlet excited state of 1-adamantylacetone noted by Gagosian, Dalton and Turro[8] is nicely accommodated using conformation A. The shorter lifetime of conformer A in its singlet state precludes much A to B isomerization, thus resulting in a large cis/trans ratio (4.9 in benzene). The cis/trans ratio from the longer-lived, conformationally equilibrated triplet biradical is much lower (1.0 in benzene).

12. Preliminary studies from our laboratory indicate that α-adamantyl-p-substituted acetophenone derivatives which lack this type of packing arrangement do not show significant cyclobutanol stereoselectivity reversals in their solid state photochemistry.

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