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STERIC EFFECTS IN THE PHOTOCONVERSION OF 2-PHENYL-2-BENZOYLBICYCLO[1.1.1]PENTANE TO 1,2-DIPHENYLTRICYCLO[2.2.0.0^{2,5}]HEXANOL. SPECTROSCOPIC EVIDENCE FOR PHENYL-PHENYL ECLIPSING.

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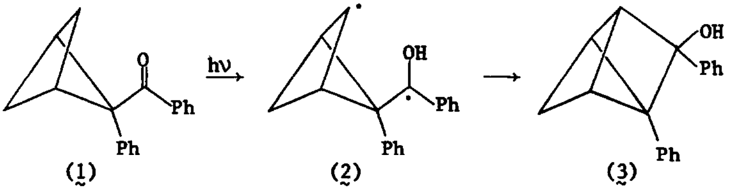
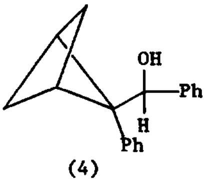
The synthetic utility of the photocyclization of alkyl phenyl ketones to cyclobutanols has been well demonstrated, particularly in the preparation of highly strained polycyclic ring systems.[1] Photocyclization is enhanced over type II elimination with α-methyl substitution. The dramatic effect observed upon substitution of an α-methyl group has been postulated from inspection of models to result from unfavorable methyl-phenyl eclipsing interactions.[1d] These interactions are expected to destabilize the transition state required for cleavage of 1,4-biradicals, especially those produced from the irradiation of α-methyl bicycloalkyl phenyl ketones. We recently reported[1a] the synthesis of a novel tricyclohexane ring system using as a key reaction the photocyclization of an α-phenyl substituted bicycloalkyl phenyl ketone. U.V. irradiation of 2-benzoyl-2-phenylbicyclo[1.1.1]pentane (1) at 313 nm in t-butyl alcohol and in benzene affords the tricyclo[2.2.0.0^{2,5}]hexanol (3) in 100% yield. Phenyl-phenyl eclipsing interactions would be expected to be very pronounced in (1) during intramolecular hydrogen abstraction and in the resulting 1,4 biradical (2) during cyclization. We have examined the quantitative effects of α-phenyl substitution and phenyl-phenyl eclipsing on the respective intramolecular hydrogen abstraction and cyclization processes of (1) and (2) and in this communication wish to report our results. We also wish to report the direct spectroscopic observation of phenyl-phenyl eclipsing in 2-(α-hydroxyphenylmethyl)-2-phenylbicyclo[1.1.1]pentane (4). Since the structure of the biradical (2) closely approximates that of the phenyl carbinol (4), the spectroscopic observation provides strong support for phenyl-phenyl eclipsing in (2).



(1) (2) (3)



(4)

The quantum yield for the photoconversion of ketone (1) to the tricyclohexanol (3) was determined in benzene to be 0.51. The photoreaction was quenched using cis 1,3-pentadiene and information concerning the triplet reactivity of (1) was calculated from a linear Sterm Volmer plot and equation 1.

$$\frac{\Phi_0}{\Phi} = 1 + Kq\tau \qquad (1)$$

From the slope of the plot (210 M^{-1}) and using 5×10^9 sec^{-1} as the value of the diffusion controlled rate constant, Kq, the triplet reactivity of (1) towards intramolecular hydrogen abstraction was calculated to be 2.6×10^7 sec^{-1}.

The rate of intramolecular hydrogen abstraction by the triplet state of (1) is substantially lower than the corresponding rates reported for similar bicycloalkyl phenyl ketones possessing no α-substituents.[2] This is somewhat surprising in light of the favorable geometry of (1) towards intramolecular hydrogen abstraction. Ketone (1) is approximately 100-400 times less reactive than exo- and endo-5-benzoylbicyclo[2.2.1]hexane,[1c] endo-2-benzoylnorbornane,[1d] and 2-benzoylbicyclo[2.2.2]octane.[1d] It is also about 5 times less reactive than the acyclic alkyl phenyl ketone, valerophenone.[3] In contrast to its relatively low triplet reactivity, the reaction quantum yield of (1) is considerably higher than the corresponding quantum yields of the above bicycloalkyl phenyl ketones ($\leq$0.20).[1c,d] Because the reaction quantum yields of bicycloalkyl phenyl ketones are dependent solely on the competitive reaction processes of the 1,4 biradicals produced from carbonyl hydrogen abstraction,[1d,3] the quantum yield for the reaction of (1) will depend on the reaction processes of (2) and will be governed by equation 2, where K_c is the rate constant for cyclization by (2) and K_{-r} is the rate constant for reverse hydrogen abstraction.

$$\Phi = \frac{K_c}{K_c + K_{-r}} \qquad (2)$$

On the basis of equation 2, and the observed data, it can be concluded that the relatively high quantum yield for the reaction of (1) is derived from less competitive reverse hydrogen abstraction from (2) ($K_c > K_{-r}$).

The diminished triplet reactivity of (1) towards intramolecular hydrogen abstraction and the relatively low rate of reverse hydrogen abstraction in (2) can best be explained in terms of unfavorable phenyl-phenyl eclipsing interactions in (1) and (2). The close proximity of the α-phenyl and benzoyl phenyl groups in (1) leads to a high degree of phenyl-phenyl eclipsing during intramolecular hydrogen abstraction. In order to minimize this eclipsing the carbonyl group, while maintaining maximum overlap of its π orbitals with those of the benzoyl phenyl, is forced to twist its nonbonding orbitals away from the γ-C-H bond. The necessity to have the γ-carbon-hydrogen bond aligned over the carbonyl nonbonding orbitals during intramolecular hydrogen abstraction has been demonstrated.[4] In an analogous manner, phenyl-phenyl eclipsing in (2) forces the C-O-H group to twist away from the γ-carbon radical center. This results in less favorable reverse hydrogen abstraction, and leads to the relatively high quantum yield. Severe phenyl-phenyl eclipsing interactions are also most likely responsible for the observed stability of (2) towards cleavage.[2]

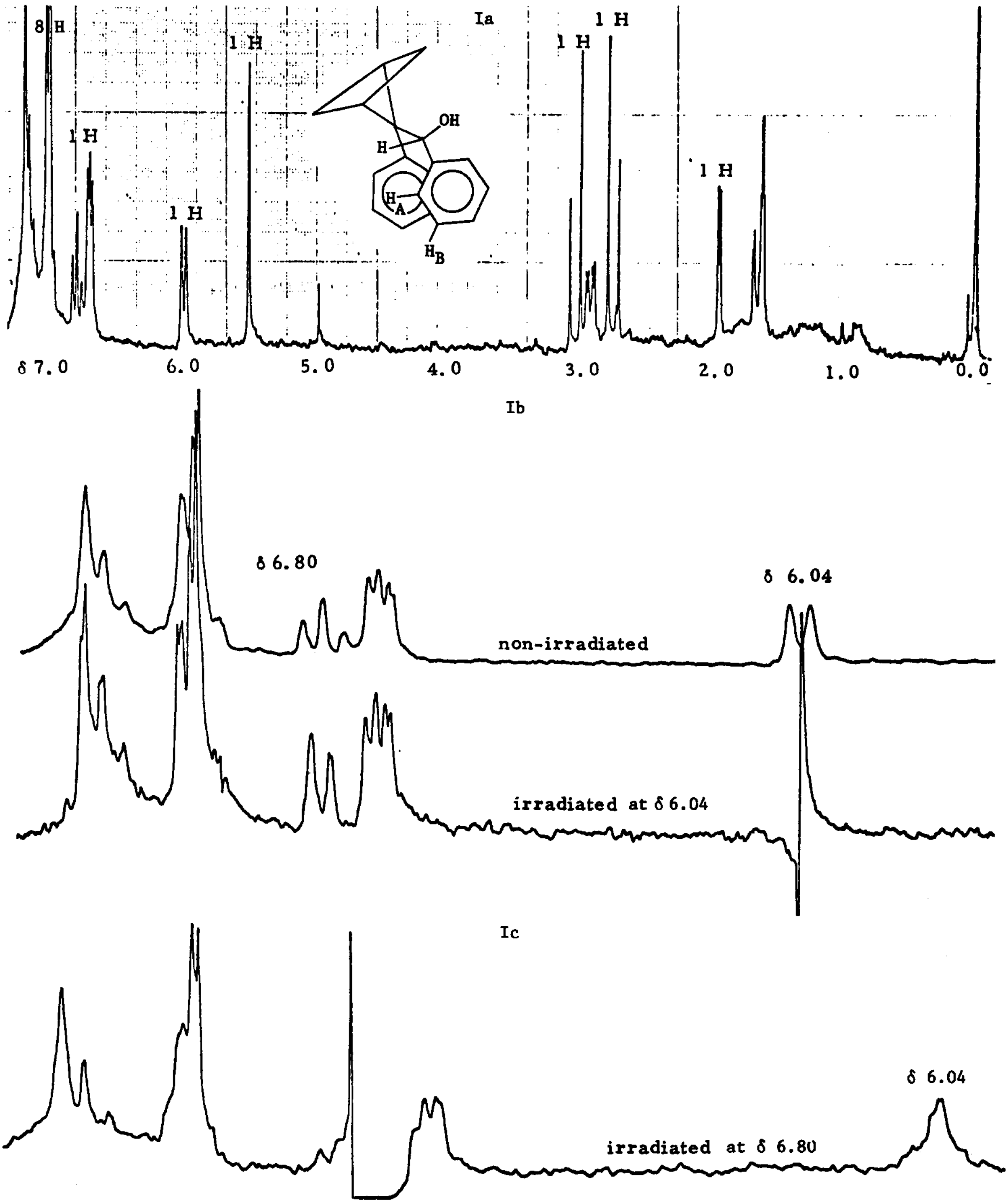


Figure I. a, NMR of 2-(α-hydroxyphenylmethyl)-2-phenylbicyclo[1.1.1]pentane (4); b, irradiation of H_B at δ 6.80; c, irradiation of H_A at δ 6.04.

Phenyl-phenyl eclipsing in (**2**) was indirectly confirmed from its spectroscopic detection in **2**-(α-hydroxyphenylmethyl)-2-phenylbicyclo[1.1.1]pentane (**4**), a reasonable model for (**2**). The NMR spectrum of (**4**) (Fig. 1a) shows a unique doublet at δ6.04 which integrates for 1 proton. The proton was assigned as the ortho phenyl proton H_A of the phenyl carbinol group, and on the basis of double resonance experiments was shown to be coupled to the meta proton H_B (δ6.80). Irradiation of the abnormally shielded proton H_A at δ6.04 markedly affects proton H_B (Fig. 1b). Irradidation of H_B at δ6.80 leads to a spectrum in which the H_A doublet is changed to a singlet (Fig. 1c). Figure 1 indicates that the most favorable configuration of (**4**) and by analogy (**2**) is one where the ortho phenyl proton of the phenyl carbinol side chain lies almost directly over the shielding zone of the adjacent phenyl ring. As a result the ortho proton is abnormally shielded and appears as a vinylic proton. Similar anisotropic effects have been observed in 2,2'-paracyclophanes where one phenyl ring is stacked directly over the other.[5] The high degree of interaction between the phenyl and phenyl carbinol groups in (**4**) and (**2**) undoubtedly results from the unique geometry of the bicyclo[1.1.1]pentane ring system.

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