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PHOTOCHEMISTRY OF 5-ALKYL-2-METHYLCYCLOHEXANONES

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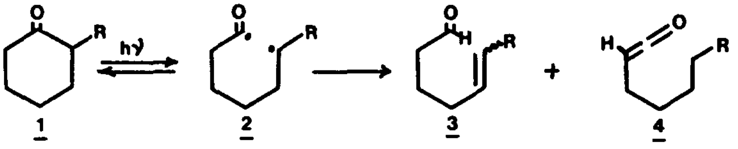
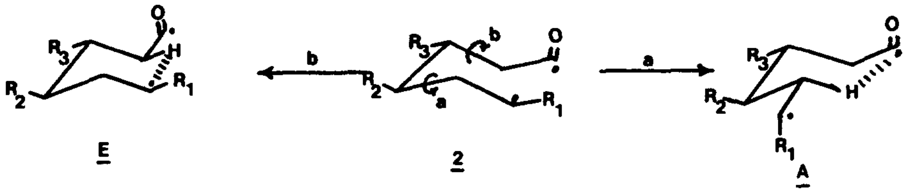
The photochemistry of alkylcyclohexanones has been rather extensively studied in recent years.[1] In most systems α-cleavage to give the more substituted biradical[2] followed by disproportunation to give enal and ketene products or recombination to give starting ketone, with epimerization in some cases,[3,4] account for the major photochemical reactions. Coyle[5], Turro[6] and Wagner[7] have discussed the effect of alkyl substitution at positions other than α- to the

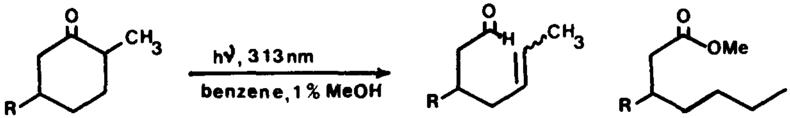


carbonyl group on the partitioning of the intermediate biradical 2 to 3 and 4. The size of the alkyl group R has little effect on the ratio of aldehyde to ketene product. However, introduction of alkyl substituents in the C_4 position decreases the yield of ketene product. The effect is most dramatic in 4-t-butylcyclohexanone (5) where less than 10% of the photoproduct is aldehyde. Chair[1,2] or preudo-chair[5] like conformations A and E have been proposed as inter-



mediates leading to enal (3) and ketene (4) products respectively. The low yield of aldehyde from 5 is accounted for by the unfavorable gauche interaction in A (R_2 = t-Bu) which makes formation of this conformation leading to enal 3 difficult. The large substituent R_2 does not appreciably affect the energy of E and ketene 4 is formed with normal efficiency.

No systematic study of the effect of large substituents at C_5 has been reported From the above considerations a large group R_3 should decrease the yield of ketene and increase the enal/ketene ratio As part of our study[8] of substituent effects on the photochemistry of cyclohexanone we have measured the quantum yields for enal and ketene formation in a series of 5-alkyl-2-methylcyclohexanones (**6**) The 2-methyl group insures that we will encounter only one mode of α-cleavage.[2] The results are given in table 1 Irradiations were carried out at



6 **7** **8**

313 nms on 0 15 M solutions of ketone in benzene containing 1% MeOH[9] and quantum yields were measured relative to 2-methylcyclohexanone (**6**a, R = H) The quantum yield for aldehyde formation from **6**a was determined to be 0.29 using benzophenone-benzhydrol actinometry [10] This value compares favorably with those in the literature (0 30[11], 0 42[7]). All samples were analyzed by gas chromatography using internal standards and corrections were made for flame-ionization detector response with authentic samples of each product. Irradiations were carried out to less than 5 per cent conversion.

Table 1

Quantum yields for photolysis of 5-alkyl-2-methylcyclohexanones

6	R	Φ_{ald}	Φ_{ester}	Φ_{sum}	Φ_{ald}/Φ_{ester}
a	H	0.29	0 13	0 42	2 3
t-b	Me(trans)	0.28	0 13	0 41	2.2
c-b	Me(cis)	0 31	0 14	0.45	2 2
c	i-Pro(trans)	0.36	0 07	0 43	5 4
d	t-Bu(c+t)	0 40	0.045	0.45	9.1

The results are consistent with our predictions. As the size of R increases the quantum yield for ester decreases and the ratio of aldehyde to ester increases. It is interesting to note that the total quantum yield for product remains unchanged even though large changes in the product ratio are observed. We have previously shown that there is much less return of the biradical in 2-methylcyclohexanone to ground state than there is for cyclohexanone and attributed this to a slower rate of recombination for more substituted biradicals.[12] The constant quantum yield for product formation from **6**a-d suggests that interconversion of conformations A and *E* must occur more rapidly than return of either to *2* where recombination is possible. In fact the total quantum yield for products may be determined by the competition between rotation of the triplet biradical out of conformation *2* and spin inversion in the biradical to a singlet state which can rapidly undergo recombination

The *cis* and *trans* isomers of *6b* were seperated by gas chromatography and irradiated separately In addition to photoproducts, epimerization was observed, consistent with the reports on 2,3-dimethylcyclohexanone[3] and 2,6-dimethylcyclohexanone[2]. The quantum yield for formation of *c-6b* from *t-6b* was measured as 0.16 giving a total quantum yield for products from *t-6b* of 0.57. A quantum yield for disappearance of *t-6b* of 0 64 was measured in close agreement with 0 57. The remaining 40% of the excited states generated can be accounted for by 1) recombination of the intermediate biradical to give back *t-6b*, 2) radiationless decay of excited *t-6b* before it forms biradical or 3) a combination of 1 and 2 While all photoproducts from alkylcyclohexanones appear to originate from the triplet state[7] and while >95% of excited cyclohexanone forms biradicals[8], the efficiency of biradical formation for methyl cyclohexanones has not been established. We are investigating this point further.

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9. Addition of 1% methanol to the benzene solutions of ketones before irradiation produces a negligible change in quantum yield for aldehyde from *5* and converts the ketene photoproduct to its methyl ester which can be analyzed by g.c.

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