

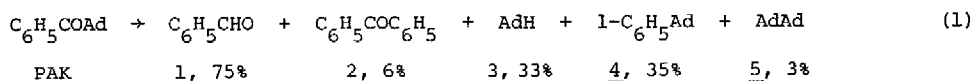
PHOTOCHEMISTRY OF PHENYLADAMANTYL KETONE IN HOMOGENEOUS ORGANIC AND IN MICELLAR SOLUTION.

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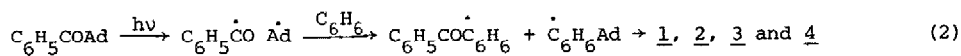
ABSTRACT: The photolysis of 1-phenyladamantyl ketone in benzene and in micellar solution has been investigated and compared.

INTRODUCTION. The photolysis of phenyladamantyl ketone (PAK, Ad = 1-adamantyl) in benzene (eq. 1) results in formation of products derived from a primary homolytic α -cleavage.¹ From the viewpoint of product structures, several issues of interest arise: (1) What is the source of hydrogen for products 1 and 3? (2) What is the source of the C₆H₅ group for products 2 and 4? In this report, in addition to addressing these questions, we investigated the photochemistry of PAK in aqueous detergent solution² in order to address the following issues: (3) How do the products of photolysis of PAK in micellar aggregates compare to those produced from photolysis of PAK in homogeneous organic solvents? (4) Which products are formed by geminate micellar cage reactions and which are formed after escape of one of the radicals from the primary geminate pair? (5) Does functionalization of the detergent backbone occur?

RESULTS. Photolysis in Benzene. PAK (7.5 x 10⁻³ M, benzene solution, vacuum degassed) was irradiated with a 450 watt Hanovia lamp (K₂CrO₄ solution filter). Products 1-5 (eq. 1) were identified by vapor chromatography. In addition, traces (~1%) of AdOH, C₆H₅C₆H₅ and C₆H₅COCO-C₆H₅ were detected. The origins of benzophenone (2) and of 1-phenyladamantane (4) are of interest, since a portion of this material might have resulted from decarbonylation of C₆H₅CO

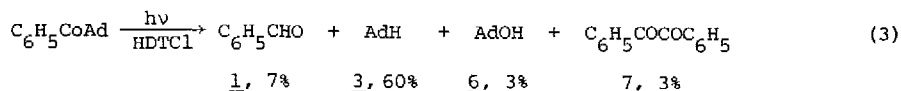


radicals, an unexpected process in solution at room temperature. An alternate route to 2 and to 4 would involve attack of adamantyl radicals and C₆H₅CO radicals, respectively, on benzene solvent. This issue was tested by photolyzing PAK in C₆D₆. The products observed under these conditions were found to be C₆D₅Ad and C₆H₅COC₆D₅ (characterized by NMR and MS), in addition to C₆H₅COD and AdD as main constituents of the benzaldehyde and adamantane formed. These observations establish that the route to 2 and 4 involves attack of radicals produced by primary α -cleavage (eq. 2) on benzene solvent, and that 1 and 3 probably result from dehydrogenation of intermediates, produced by radical addition to benzene.



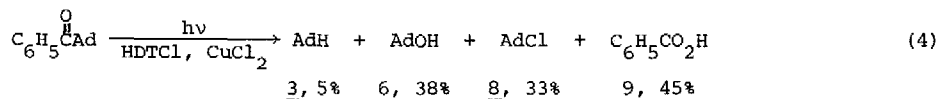
Photolysis in Micellar Solution Without Scavengers. PAK (4.75 x 10⁻³ M) in 0.05 M aqueous hexadecyltrimethylammonium chloride, HDTCl, was photolyzed under conditions comparable to those

described above. In addition to small amounts of 1 and 7, we find that adamantane (3) is the main product identifiable by vpc analysis (eq. 3). In contrast to the good mass



balance obtained in benzene solution, only the adamantyl moiety is well accounted for in the volatile products. It thus appears that the $\text{C}_6\text{H}_5\dot{\text{C}}\text{O}$ radical has attacked and become bonded to the detergent backbone. This possibility is consistent with the observation that detergent which was employed in the photolysis could be recovered and purified and was found to possess an absorption characteristic of a $\text{C}_6\text{H}_5\text{COR}$ function. Assuming that the extinction coefficient of the functionalized detergent is equal to that of $\text{C}_6\text{H}_5\text{CO}(\text{CH}_2)_9\text{CH}_3$, the yield of functionalized detergent is computed to be 12% (based on the PAK consumed) bringing the total mass balance for the $\text{C}_6\text{H}_5\dot{\text{C}}\text{O}$ moiety to 26%. When D_2O rather than H_2O was employed as solvent no incorporation of D in products was observed.

Photolysis in Micellar Solution with Cu^{2+} as a Selective Aqueous Phase. In order to differentiate the products occurring via geminate, non-scavengable micellar cage reaction from the products occurring via after micellar cage escape, the photolysis of PAK in HDTCl solutions containing CuCl_2 (1.7×10^{-2} M) was investigated. It has been shown that Cu^{2+} is a selective scavenger of radicals in the aqueous phase, but that Cu^{2+} does not scavenge geminate radical pairs in micelles.^{3,4} It can be seen that the product distribution (eq. 4) is changed dramatically from that observed when Cu^{2+} is absent. Adamantane (3) becomes a minor product and mono-substituted adamantane AdOH (6) and AdCl (8) become the major products derived from the Ad moiety of PAK. Furthermore, no functionalization of the detergent side chain by the $\text{C}_6\text{H}_5\dot{\text{C}}\text{O}$ moiety can be detected. Instead, benzoic acid (9) is found as a significant product.⁵



DISCUSSION. The products produced by photoexcitation of PAK differ substantially as a function of the photolysis medium. In benzene (eq. 1) the solvent is an active participant in the overall reaction and serves to trap radicals and donate hydrogen atoms (via intermediates formed by addition of radicals). In micellar solution (in the absence of CuCl_2 scavenger) the major processes evidently involve hydrogen abstraction from the detergent backbone, whereas in the presence of scavenger the major products derive from reaction of Ad and $\text{C}_6\text{H}_5\dot{\text{C}}\text{O}$ radicals which escape from the micelle into the aqueous phase and react with CuCl_2 .

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3. N.J. Turro, B. Kraeutler and D. Anderson, *J. Am. Chem. Soc.*, **101**, 7435 (1979).
4. Variation of the CuCl_2 concentration from 2×10^{-2} M to 8×10^{-3} M had no effect. Thus, the scavenging of escaping $\text{C}_6\text{H}_5\dot{\text{C}}\text{O}$ and Ad radicals is 100% efficient.
5. Benzoic acid was determined by esterification of the reaction mixture with ethanol, followed by extraction of ethylbenzoate and quantitative VPC analysis.

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