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UNUSUAL PHOTOCHEMICAL REDUCTION AND DEACYLATION OF NAPHTHYL KETONES INCORPORATED IN A TRIPTYCENE SKELETON

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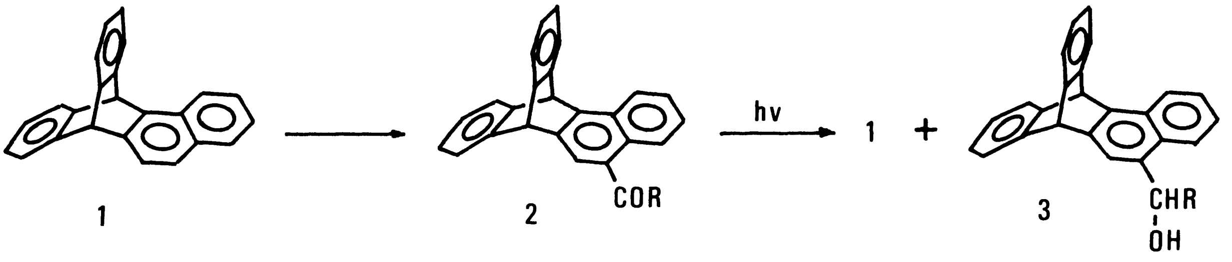
In contrast with the photochemical inertness of acetonaphthones, irradiation of the 5-acetyl, propionyl, butyryl, and decanoyl derivatives of 7,12-dihydro-7,12-(o-benzeno)benz[a]anthracene in methanol gave the corresponding reduction products and the deacylation product in efficiency of 0.02 - 0.05.

The photochemical rearrangement of triptycenes <u>via</u> the carbene intermediate has been shown to be a typical example in which the reaction path deviates from the representative di-π-methane mechanism.1) Since this rearrangement is very widely applicable to the triptycenes carrying the substituents either at the bridgehead or on the aromatic ring to give novel ring systems of interest,2) we thought it worthwhile to determine whether comparable chemistry might occur in a series of related triptycenes with naphthalene chromophore. It is well established in the barrelene derivatives that the excited triplet states approximately localized in the naphthalene and anthracene chromophores can induce the di-π-methane rearrangement.3) Instead of the expected photorearrangement of the triptycene skeleton, we encountered the unusual reduction and deacylation which occurred upon irradiation of the 5-acyl derivatives (**2**) of 7,12-dihydro-7,12-(o-benzeno)benz[a]anthracene (**1**). We wish to report here this novel channel for the light-wastage of the excited state ketones.4)

Irradiation of **1** in methanol under an argon atmosphere with Pyrex filered light for 7 h gave no significant change in the solution. Vycor-filtered light gave after prolonged irradiation some unidentified polymeric product which showed no meaningful signal in its ^{1}H NMR spectrum. Neither the expected ether nor hexacyclic hydrocarbon was found.5)

The Friedel-Crafts acylation of **1** gave the corresponding 5-acyl derivatives as the sole products. Irradiation of a 1 mM solution of 5-acetyl derivative **2a** in methanol with Pyrex filtered light gave 5-(1-hydroxyethyl) derivative **3a** (12 %), deacetylation product **1** (2.5 %) and 11 % of starting material **2a** back.6) Similar irradiation of 5-propionyl, 5-butyryl, and 5-decanoyl derivatives **2b** ~ **2d** gave corresponding reduction products **3b** ~ **3d** in addition to deacylation product **1**. Quantum yields of conversion and product formation for these reactions are

Scheme 1



	R
a	CH_3
b	CH_2CH_3
c	$CH_2CH_2CH_3$
d	$(CH_2)_8CH_3$

Table 1. Quantum Yields of Conversion and Product Formation for Irradiation of 2[a], 7)

	Φ_{-2}	Φ_3	Φ_1
2a	0.30	0.024	0.020
2b	0.17	0.023	0.026
2c	0.19	0.032	0.048
2d	0.12	0.037	0.040

[a] Conversion < 30 %. Product analysis was by HPLC. 1 mM in methanol.

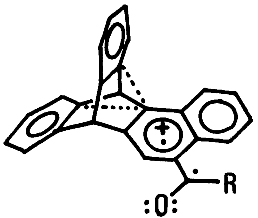
summarized in Table 1.7)

Photolysis of 2c and 2d did not give 2a which might have been formed by the type II photoelimination. Irradiation of 2a and 2c in benzene gave only 1 with a low efficiency but in moderate yields (20.6 and 34.4 %, respectively) without any reduction product. When 1,3,5-hexatriene (0.25 mM) was added to a methanol solution of 2a (1 mM), the deacylation was affected only to a small extent but the photoreduction was considerably suppressed from the 12 to 2 % yield.

The photoreduction of 2a ~ 2d is quite an unexpected reaction in view of the fact that both 1- and 2-acetonaphthones are not photoreduced in methanol either to the corresponding alcohols or to the pinacols under our experimental conditions, although the quantum yield in the pinacol formation from the acetonaphthones is reported to be 0.001 in isopropyl alcohol.7) The photodeacylation of alkyl aryl ketones is not a popular reaction either, albeit not without precedent. Acetophenone undergoes deacetylation when irradiated with full mercury arc in dilute solution in alkanes.8) The α-cleavage of acetophenone in the gas phase takes place from the vibrationally excited T_1 state when the molecule is excited to the S_2 or S_3 states.9) However, no such reaction has been reported to our knowledge for the photolysis with the light of longer wave length in the condensed phase.

The remarkable difference in photoreactivities between acetonaphthones and 2a ~ 2d might have been easily explained if there were difference in the nature of the lowest triplet states, since the aromatic ketones with $T_1(n, \pi^*)$ are characterized by their capability in photoreduction. This turns out not to be the case, since 2a in a EPA glass appears to have the lowest $T_1(\pi, \pi^*)$ state of 53 kcal mol^{-1} which is lower-lying than that of 57 kcal mol^{-1} of 1-acetonaphthone. The spectra of 2a showed no distinct vibrational fine structure and had the life-time of 1.2 s at 77 K.[10] The preliminary quenching study with 1,3,5-hexatriene (E_T = 48 kcal mol^{-1}) showed that this lowest triplet state should be responsible at least for the photoreduction of 2a. Further analysis would be necessary to see how the n,π^*-like reactivity is incorporated in the $T_1(\pi, \pi^*)$ state of 2a ~ 2d.

There are some circumstantial evidences which suggest the presence of another state which may be responsible for the deacylation reaction. The added 1,3,5-hexatriene did not show noticeable effect on the reaction. Weak fluorescence was observed at 415 nm for 2a, suggesting enough life-time for the photocleavage. An initial alkyl-CO cleavage is expected on simple energetic grounds, since this reaction to form ArCO· ·R is less endothermic than Ar· ·COR. Decarbonylation of the benzoyl radical requires activation energy as high as 28.4 kcal mol^{-1},[11] and therefore, the alkyl-CO cleavage followed by decarbonylation of the naphthoyl radical is not very likely. We feel it would be possible for π,π^* states of 2 which must have some CT character when incorporated in the electron-donating triptycene skeleton (see 4) to undergo the aryl-COR cleavage.



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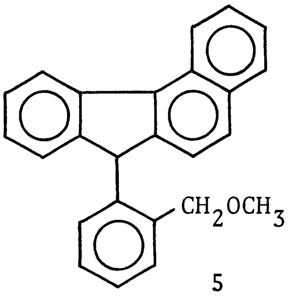
5) 5 and 6 are some of the candidates for the expected products, as α-bonding appears to be preferred to β-bonding in the excited state naphthalene.[3]



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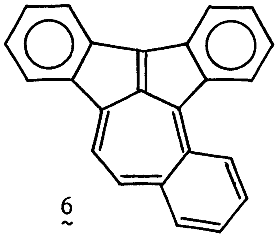

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6) The structure of the rest of the reaction mixture could not be determined, since neither HPLC nor NMR gave any signal other than those due to **1**, **2** and **3**.

7) Quantum yield of disappearance of p-methoxyacetophenone in isopropyl alcohol was taken as a reference. See: G. Porter and P. Suppan, Trans. Faraday Soc., **62**, 3375 (1966).

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