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PHOTOREDUCTION OF FLUORENONE BY AMINES. MEDIUM EFFECTS.

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We have reported that aliphatic amines are efficient photoreducing agents for aromatic ketones (1-4) which have low-lying n,π* triplet states. (5) We have also found that p-aminobenzophenone, PAB, which is not photoreduced by 2-propanol because of a low-lying chemically unreactive π,π* or charge-transfer (CT) triplet in that solvent (6,7), is photoreduced readily by triethylamine in cyclohexane (8a,b,c), $\varphi \sim 0.6$. We wish to report on a study of fluorenone, which does not have CT absorption, is reported to have a low-lying π,π* triplet (6,9), and is not photoreduced by alcohols. (10) Its photoreduction by N,N-dimethylaniline has been reported, without quantum efficiency. (11)

Solutions were degassed by the freeze-thaw procedure and irradiated in Pyrex under argon, with a Bausch and Lomb 38-86-01 grating monochromator, Osram SP-200 lamp, or on a turntable with GE H-85-A3 lamp. Analyses for residual ketone were made from the absorbance at 380 mμ. Quantum yields were determined on the monochromator with a ferrioxalate actinometer. (12)

We confirm that fluorenone is not photoreduced in 2-propanol, and we find that it is also essentially unaffected when ~ 0.03 $\underline{M}$ solutions are irradiated at 404 mμ in cyclohexane and in 0.1 $\underline{M}$ 2-propanol and in 0.005 $\underline{M}$ fluorenol in cyclohexane. Fluorenone (0.03 $\underline{M}$) is photoreduced at 404 mμ by a primary amine, 2-butylamine, with low efficiency, $\varphi \sim 0.04$ in neat amine, and $\varphi \sim 0.02$ in 0.10 $\underline{M}$ amine in cyclohexane. It is photoreduced slightly more efficiently by a secondary amine, N-methyl-2-butylamine, $\varphi \sim 0.05$ in the neat amine, and $\varphi \sim 0.13$ in 0.08 $\underline{M}$ amine in cyclohexane. Fluorenone is photoreduced by triethylamine, and the reaction both in neat amine and in 1.3 $\underline{M}$ amine in cyclohexane appears to lead to products expected from coupling and cross-coupling of the 9-hydroxy-9-fluorenyl and 1-diethylamino-1-ethyl radicals. Fluorenone pinacol was isolated, mp 195-197° dec, lit. (13) 190-192° dec. The cross-coupling product, was isolated, mp 128-129°. Anal. Calcd for $C_{19}H_{23}ON$: C, 81.10; H, 8.24; N, 4.98. Found: C, 81.16; H, 8.30; N, 4.77 (Dr. Nagy). A dramatic effect of medium on quantum yield is observed when the tertiary amine is diluted with cyclohexane, Table 1.

Table I

Photoreduction of 0.03 M Fluorenone by Triethylamine.

Effect of Cyclohexane on Quantum Yield.

Et_3N, M	φ
7.23 (neat)	0.094[a]
1.95	0.19[a]
1.00	0.37[a]
0.50	0.69[a]
0.198	0.92[b]
0.099	0.91[a,b]
0.071	0.85[b]
0.043	0.76[b]
0.018	0.60[b]

a. Irradiation at 404 mμ, quantum yield by actinometry.

b. Tubes were irradiated simultaneously on turntable and relative rates were determined; ferrioxalate actinometry was determined on one sample at 404 mμ.

The quantum yield for photoreduction of fluorenone rises ten-fold to 0.91 as the neat amine is diluted down to 0.1 M in cyclohexane, and decreases very slowly with further dilution. The inverse plot of the latter data leads to a hypothetical limiting quantum yield of 1.0, and k_d/k_r = 0.013 M, a very low favorable ratio of rate constant for deactivation to that for abstraction. Study of quenching by 0.12 to 1.8×10^{-2} M trans-stilbene of photoreduction of 0.03 M fluorenone in 0.10 M triethylamine in cyclohexane leads to a linear plot of $1/\varphi$ vs. concentration of quencher, $k_q/k_r = 140$, $k_r = 1.7 \times 10^{7}$ M^{-1} sec^{-1} based on an adjusted quenching constant (14)

$k_q = 2.4 \times 10^9\ \underline{M}^{-1}\ sec^{-1}$, and $k_d = 2.2 \times 10^5\ sec^{-1}$. During the quenching trans-stilbene is isomerized to cis-stilbene. A similar quenching study leads to $k_r = 2.2 \times 10^6\ \underline{M}^{-1}\ sec^{-1}$ for abstraction by fluorenone triplet from N-methyl-2-butylamine in cyclohexane.

Both a protic solvent and a dipolar aprotic solvent have an effect opposite to that of the hydrocarbon, and fluorenone is essentially not photoreduced in dilute solutions of triethylamine in 2-propanol and in acetonitrile. These medium effects parallel those observed in photoreduction of PAB by triethylamine. (8) In that case increased reactivity was attributed to inversion of triplet energy levels and formation of the n,π* triplet in non-polar media. (7,8) Hydrocarbon diluent may also make photoreduction more efficient by decreasing light-absorbing transients, (3,8c) but we do not find such an effect in the fluorenone system. Fluorenone may be reacting in hydrocarbon medium via a triplet with much n,π* character. (15) This may react efficiently with a tertiary amine via an electron transfer mechanism, (8,3) eq. 1. This triplet may not be sufficiently energetic to react efficiently with primary and secondary amines and alcohols in hydrocarbon medium.

$$>C{=}O + >\ddot{N}\text{-}CH< \rightleftarrows [>\dot{C}\text{-}\overset{..-}{O}: \quad >\overset{\cdot+}{N}\text{-}CH<] \rightarrow >\dot{C}\text{-}OH + >\ddot{N}\text{-}\dot{C}< \qquad (1)$$

The reaction of fluorenone in oxetane reactions with olefins (15) and with a ketenimine (16) may also be consistent with reaction via an n,π* type triplet. One may not rule out that the reactions of fluorenone proceed via π,π* triplets which are made less reactive in polar media by hydrogen-bonding or dipole-dipole interaction. We find that 2-acetonaphthone, which shows low reactivity in the oxetane reaction, (15,16) and meta-aminobenzophenone show only low reactivity in triethylamine-cyclohexane. This may result from the failure of their triplets to acquire substantial n,π* character.

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