Tetrahedron Letters, Vol 32, No 32, pp 3915-3918, 1991
Printed in Great Britain

0040-4039/91 $3.00 +
Pergamon Press plc

Photocyclization of Ortho-Benzoyl N-Alkylanilinium Ions

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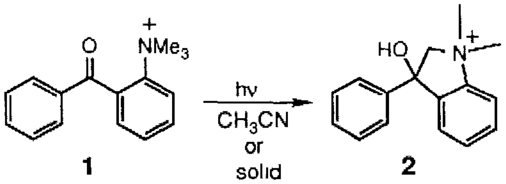
Abstract: *Ortho-benzoyltrimethylanilinium tetrafluoroborate efficiently photocyclizes by triplet state δ-hydrogen abstraction to the 1,1-dimethyl-3-hydroxy-3-phenyl-2,3-dihydroindolium salt both in acetonitrile solution and as a solid Ortho-benzoyl-N,N-dibenzylaniline hydrochloride photocyclizes in acetonitrile to N-benzyl-2,3-diphenylindole. The rate constant for δ-hydrogen abstraction is high thanks to a favorable geometry but rapid internal quenching lowers the quantum yield to only 0 02. Both reactions proceed essentially quantitatively.*

Ortho-alkoxyphenyl ketones[1-3] and o-tert-butylphenyl ketones[4] undergo δ-hydrogen abstraction from their triplet states to generate 1,5-biradicals that cyclize to benzofuran or indanol derivatives,[5] the former in synthetically useful yields[3] Attempts to prepare indoles by comparable photocyclizations of o-alkylamino phenyl ketones have not been successful, messy mixtures usually being the result[6] Rapid electron transfer from nitrogen to carbonyl, both inter- and intramolecular, competes with and impedes hydrogen abstraction. Acylation of α-aminoketones suppresses CT quenching and promotes normal photoreactivity[7] However, o-amidobenzophenones undergo primarily photolytic deacylation and dealkylation.[8] Despite Padwa's bad luck with α-aminoacetophenones,[7a] we felt that tying up the lone pair on nitrogen by quaternization or protonation could promote cyclization and now report the first examples of high yield photocyclization involving intramolecular hydrogen abstraction from o-benzoyl anilinium salts.

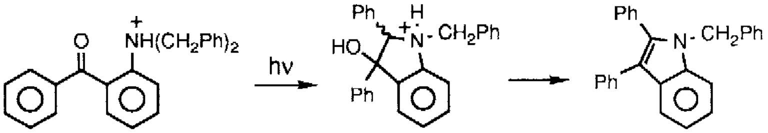
Ortho-benzoyltrimethylanilinium tetrafluoroborate **1** was prepared by alkylation of o-aminobenzophenone with excess methyl iodide followed by ion exchange with $AgBF_4$. Near uv irradiation[9] of either dilute acetonitrile solutions or crystals of **1** resulted in its quantitative transformation to 1,1-dimethyl-3-hydroxy-3-phenyl-2,3-dihydroindolium tetrafluoroborate **2**.[10] The product was isolated by recrystallization from methanol. Its NMR spectrum closely resembles that of the indanol formed from the isoelectronic o-tert-butylbenzophenone OTBBP,[3] except for differences in chemical shifts due to the positive nitrogen. The material balance was within experimental error of 100% The solid product appears to be indefinitely stable. Aoyama reported very low chemical yields and quantum efficiencies for the photocyclization of o-dimethylaminobenzophenone.[6] In contrast, **1** yields **2** with a quantum efficiency of 0.56 in acetonitrile



1 **2**

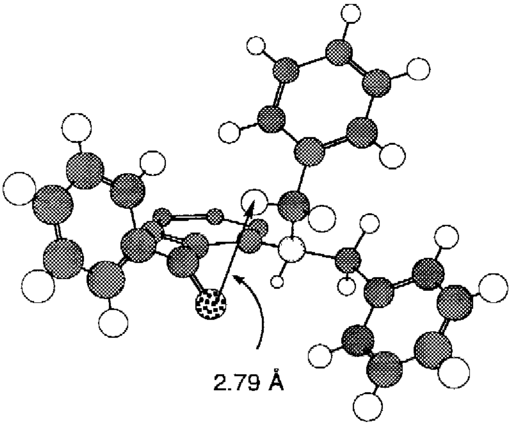
The reaction is readily quenched with typical triplet quenchers. Quantitative studies were performed by measuring the effect of added ethyl sorbate on the loss of **1** as indicated by the change in carbonyl IR absorption at 1680 cm^{-1} A linear Stern-Volmer plot gave a $k_q\tau$ value of 160 ± 40 M^{-1}. UV analysis proved to be inaccurate, since a minor byproduct absorbs strongly in the monitoring region. With a value for k_q in acetonitrile of 1×10^{10} M^{-1} s^{-1},[11,12] we calculate a triplet lifetime of 16 ± 4 ns We assume that the reaction proceeds by δ-hydrogen abstraction and then cyclization of the 1,5-biradical intermediate, as occurs in OTBBP.[4] The triplet lifetime of OTBBP is only 0.5 ns in hexane.[4] The positive charge on nitrogen has the expected effect[13] of slowing down δ-hydrogen abstraction, but the 30-fold effect is much smaller than the 1000-fold reactivity difference between protonated γ-dimethylaminobutyrophenone and valerophenone.[14] The positive charge in **1** deactivates the adjoining C—H bond towards an electron-deficient reagent; but it also enhances the intrinsic reactivity of the carbonyl with which it is conjugated. This conclusion is in accord with our earlier finding that protonation of pyridyl ketones increases their triplet reactivity by a factor of ten.[15]

o-Benzoyl-N,N-dibenzylaniline hydrochloride **3** also undergoes photocyclization in acetonitrile solution to yield N-benzyl-2,3-diphenylindole, which was identified by x-ray crystallography. Quantum yields were readily measurable by HPLC and were low: 0.02 in dry acetonitrile and 0.001 with 6% water present. The indole accounts for all initial reaction but itself is gradually converted to an as yet unidentified secondary product. Quenching studies with ethyl sorbate provided a $k_q\tau$ value of 2 4 M^{-1} and thus a triplet lifetime of only 0.25 ns These figures indicate a rate constant for hydrogen abstraction of 8×10^7 s^{-1}, comparable to that for **1** The low quantum yields indicate a rapid competing quenching process. Two possibilities are likely·



3

the strongly acidic triplet anilinium ion can decay by deprotonatation; and rapid proton transfer to the carbonyl oxygen probably occurs, as in o-hydroxy ketones[16] Uv spectra indicate that in solution the ground state anilinium ion is in equilibrium with its weak conjugate base, which is a powerful internal filter. This dissociation is enhanced by added water, which explains the lowered quantum yields



It is noteworthy that triplet **3** abstracts a δ-hydrogen more rapidly than does o-benzyloxybenzophenone **4**,[2] despite the positive nitrogen The lowest energy conformation for **3** predicted by MMX calculations is pictured on the left. The N-H is within hydrogen bonding distance of the carbonyl oxygen and one benzylic hydrogen is only 2.8 Å away, close enough to react rapidly[17] Unlike **3**, **4** exists primarily in an unreactive conformation with the benzyl group held anti to the carbonyl[2]

Simple monoalkyl o-benzoylanilines undoubtedly mimic the o-alkoxy ketones and exist primarily in conformations that cannot undergo internal hydrogen abstraction, with the N-alkyl group twisted away from the carbonyl.[2] We looked at the N-benzyl case: it does not photocyclize in acetonitrile containing acids as strong as triflic. The combination of lowered intrinsic reactivity because of the positive charge, low population of reactive conformations, rapid radiationless decay by deprotonation, and probable internal filtering by unprotonated amine make efficient cyclization in these cases unlikely. Nonetheless, the successful cyclization of di- and trialkylanilinium salts suggests several avenues for further exploration.

Acknowledgement. This work was supported by NSF grant CHE 88-15052. The NMR was purchased with NSF grant No CHE 88-00770.

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(9) Samples were irradiated either at 313 nm or through a Pyrex filter

(10) White crystals, mp 194-195°; MS m/z 240 (parent), IR (KBr) 3500 cm^{-1}; ^{1}H-NMR (CD$_3$CN) δ 3.59 (s, 3 H), 3.67 (3 H, s), 4 11 (dd, J = 12.7, 0.9 Hz, 1 H), 4.38 (d, J = 12.7 Hz, 1 H), 4 77 (d, J = 1.5 Hz, 1 H, OH), 7.26 (dd, J = 7.5, 1.3 Hz, 1 H), 7 4-7 5 (m, 5 H), 7.65 (td, J = 7 5, 1 3 Hz, 1 H), 7.73 (td, J = 8.2, 1.3 Hz, 1 H), 7.78 (br d, J = 8.2 Hz, 1 H); ^{13}C-NMR (CD$_3$CN) δ 55.8, 59.7, 81.3, 81 5, 118.7, 127.3, 127.5, 129.6, 129 8, 132.9, 132.1, 139.6, 141.2, 148.7.

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(Received in USA 18 March 1991)