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(Co)oxidation/cyclization processes upon irradiation of triphenylamine

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ABSTRACT

Irradiation of triphenylamine (Ph_3N) in nitrogen-flushed solution leads to 9-phenylcarbazole and two tetrahydroderivatives (1,2,3,4- and 1,2,7,8-) via disproportionation of the corresponding 4a,4b-dihydrocarbazole. In oxygen-equilibrated solution oxidative cyclization occurs through the intermediacy of a triplet peroxy diradical, which either abstracts a hydrogen atom intramolecularly or (mainly) cleaves back to the reagents. The role of the key intermediates is supported by DFT calculations and by trapping by triarylphosphines (that are thus efficiently oxidized, while preventing the cyclization of Ph_3N). The hydroperoxide, on the other hand, causes inefficient co-oxidation of sulfides.

The electrocyclic rearrangement of stilbene and related aryl-alkenes is of great interest both as a synthetic approach to polycyclic derivatives and for the mechanistic issues involved.[1] This is probably the most in-depth studied reaction where photochemical and thermal processes follow opposite stereochemical courses,[1a] leading to either *trans* or *cis* relationship of the substituents at the ring fusion positions. When these are hydrogen atoms, oxidation may follow and leads to an aromatic derivative.[1c] Heteroatom-containing analogs of stilbene and other 6π electrons systems have been likewise studied intensively and are of equal interest on the same grounds. An example is the photocyclization of di-[2–4] and tri-phenylamines[3–5] that leads to dihydrocarbazoles, some of which are present among natural products,[6] or, by oxidation, to carbazoles, a class of heterocycles often employed in drugs,[7] dyes,[8] photoactive polymers,[9] and, OLEDs.[10] In particular, the photocyclization of triphenylamine (see Scheme 1) to 9-phenylcarbazole (**NPC**) has been reported[2e,3] in different organic solvents. From the mechanistic point of view, electrocyclic photocyclization is one of the few cases where the adiabatic course of a photoreaction (from the excited state of the reagent to the excited state of the product) has been documented. Thus, both time resolved spectroscopy analyses[5,11] and a computational investigation by the AM1-SCI method supported that cyclization from $^3Ph_3N$ (singlet–triplet intersystem crossing is almost quantitative in this compound)[2e,3] led to trans-*N*-phenyl-4a,4b-dihydrocarbazole in the triplet state (represented by the diradical formula $\mathbf{^3DHC}$,[11] *path a*, Scheme 1) and this in turn crossed (*path b*) over to the singlet ground state, more stable by 3.9 kcal mol^{-1} (represented as $\mathbf{DHC_0}$).[12] The last intermediate had a zwitterionic rather than diradical character and it was remarked that this was consistent with the fact that no spin trapping occurred in the presence of 5,5-dimethyl-1-pyrroline-*N*-oxide and *N-tert*-butyl-α-phenylnitrone.[11,13] It was formed efficiently, but mainly reverted back to Ph_3N (*path d*, >90%) and only in part underwent disproportionation (*path c*) to carbazole (NPC) and a tetrahydrocarbazole ($\mathbf{H_4}$**-NPC**, of structure not known, notice that analogous *N*-methyldiphenylamine[2a] gives the 1,2,7,8-derivative).

In the presence of oxygen, aromatization of $\mathbf{DHC_0}$ to **NPC** occurred. It was found that the quantum yield of the oxidative cyclization (Φ_{cy}) increased from 0.04 to 0.09 (depending on the nature of the solvent) when changing from oxygen-free conditions to ca. 0.2 in air equilibrated solution.[3] Potentially, oxygen may interact with all of the sequentially formed intermediates, $\mathbf{^3Ph_3N}$, $\mathbf{^3DHC}$, and $\mathbf{DHC_0}$, and the overall yield appeared to result from the balance between quenching of $^3Ph_3N$ by molecular oxygen (producing $^1O_2$, with $\Phi = 0.63$ in benzene)[14] and the intervention of O_2 mediated paths making more efficient the formation of **NPC**. Hydrogen peroxide was also formed.[3] Understanding the role of oxygen in the aromatization step deserved, we thought, further attention, also because it seemed possible that some intermediates generated may oxidize other compounds under mild conditions. In view of the above, we decided to further pursue this issue and report

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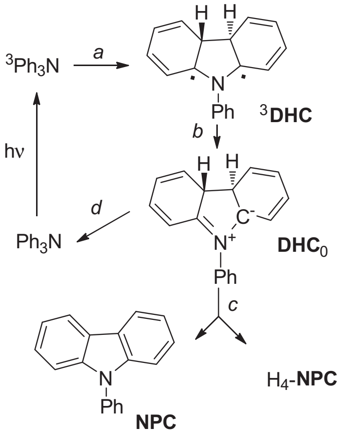


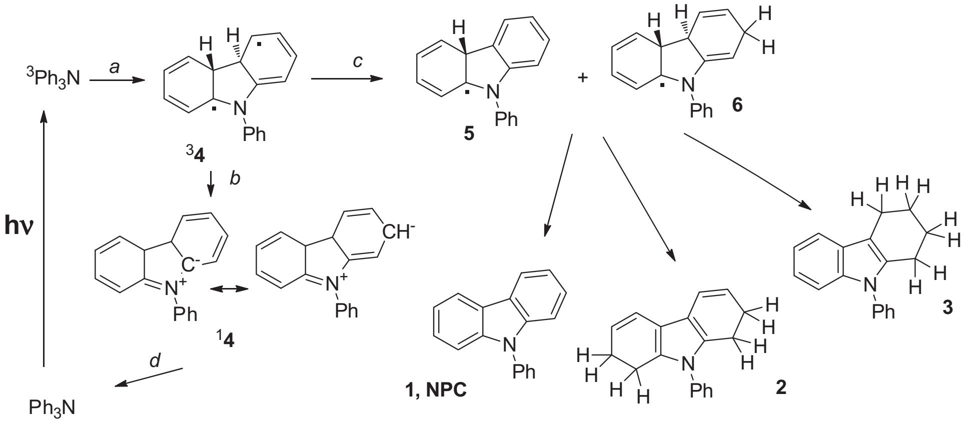
Scheme 1. Photochemical cyclization of triphenylamine (Ph_3N).

below a combined experimental and computational investigation about the photocyclization of triphenylamine in different solvents and in the presence of oxidation-liable substrates.

In our hands, irradiation of a nitrogen-flushed 1×10^{-2} M acetonitrile solution of Ph_3N led to *N*-phenylcarbazole (**1**) as the main product (53%) along with two tetrahydro-derivatives that were spectroscopically identified (see Scheme 2) as *N*-phenyl-1,2,7,8-tetrahydro- (**2**, 14%) and *N*-phenyl-1,2,3,4-tetrahydrocarbazole (**3**, 5%), containing respectively a doubly conjugated pyrrole and an indole aromatic system. Compounds **1**–**3** obviously arose from a dihydrocarbazole intermediate (**4**) the role of which was assessed by means of a DFT computational study at the (U)B3LYP level of theory, by using the integral equation formalism model (IEFPCM) for the solvent (acetonitrile). The Pople's basis set 6-311++G(2d,p) was adopted for all atoms (see ESI† for further details). This essentially confirmed the AM1-SCI results, though with some differences in the electronic distribution. Thus, singlet ^{1}**4** had a purely zwitterionic character (a mixture of two predominant mesoionic structures, as indicated in Scheme 2) and lay a mere 3.4 kcal mol^{-1} below the triplet ^{3}**4** (of diradical character, satisfactory represented by the single formula in Scheme 2). As mentioned, rearrangement to ^{3}**4** and ISC to ^{1}**4** mainly led to retro-cyclization to triphenylamine (*path d*). No intramolecular concerted path leading to an aromatic system was available and reasonably intermolecular hydrogen transfer took place leading to radicals **5** and **6** and to the observed products **1**–**3** from them.

The corresponding experiment with an oxygen-equilibrated solution gave **1** as the only isolated product, along with a small amount of highly polar products. In order to understand the mechanism of the oxidative photocyclization, the photoreaction of Ph_3N in the presence of potential oxygen acceptor was investigated. Sulfides and phosphines were chosen as suitable probes (see Scheme 3). The results are reported in Tables 1 and 2 and can be summarized as follows. Sulfides were co-oxidized to sulfoxides at a rate dependent on structure and conditions. The rate of the triphenylamine oxidative cyclization increased to a various extent (10–250%) and the rate ratio of sulfoxide versus carbazole formation was $\geqslant 1$ (from ca. 1.1 to 2.5). In contrast, irradiation of triphenylamine in the presence of either triphenylphosphine or tris-(2-methylphenyl)phosphine led to the corresponding phosphine oxides, but at the same time the formation of *N*-phenylcarbazole (**1**) was completely inhibited. A precise comparison between the oxidation rate of sulfides and phosphines was not feasible, since different irradiation conditions had to be adopted to avoid autooxidation of phosphines, but it was clear that the photooxidation of the latter substrates was at least five times faster than either oxidation of sulfides or oxidative photooxidation of TPA alone. These results pointed to the involvement of different intermediates in the reaction of the two traps.

Energy transfer to give singlet oxygen is energetically viable only by quenching of $^3Ph_3N$ (see above)[14] and not from ^{3}**4**, due to the low energy gap of the latter from ground state ^{1}**4**, much below that required for $^1O_2$ formation (ca. 22 kcal mol^{-1}).[15a] If these were the only effect by oxygen, it would lead to quenching of the cyclization and oxygenation of the additives.[15b,c] The following evidences suggested that this was not a singlet oxygen reaction, however: (1) thus, under bona fide $^1O_2$ conditions, ring-substituted triphenylphosphines are known to give phosphinates along with phosphine oxides,[16] contrary to what observed in the present case (see Table 1); (2) as for sulfides, sulfones are known to always accompany the sulfoxides, at least in polar aprotic and non-polar solvents, and benzyl sulfides do undergo both sulfoxidation and oxidative cleavage to benzaldehyde in protic media, again differently from what observed under the present conditions (see Table 2).[17] An alternative mechanism is that the diradical character of dihydrocarbazole ^{3}**4** makes viable a chemical quenching of the intermediate by molecular oxygen (*path e* in Scheme 3). Actually, the interaction of ^{3}**4** with ground state (triplet) oxygen can result in a singlet, a triplet, or a quintet. Computing the energy of all of the possible combinations demonstrated that the most favored path led to a chemically bonded adduct with triplet multiplicity that was formed through an almost thermoneutral process ($\Delta G° = 0.24$ kcal mol^{-1}, through a transition state that was located at 6.7 kcal mol^{-1},see Scheme 4). More precisely, taking into account both the regiochemistry and the stereochemistry of such



Scheme 2. Cyclization of Ph_3N under O_2-free conditions.