

On the Photochemical Synthesis of *N,N'*-Dimethylindolo[2,3-*c*]carbazole and the Mechanism of Its Formation from *N,N'*-Dimethyl-*N,N'*-diphenyl-1,4-phenylenediamine

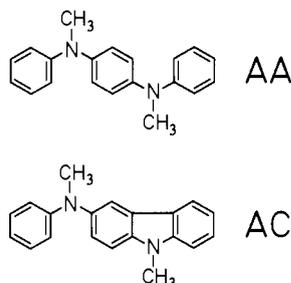
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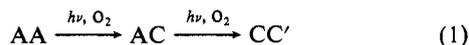
Abstract: Of the five possible indolocarbazoles the title compound (CC) is the only unknown isomer. It is easily prepared photochemically from *N,N'*-dimethyl-*N,N'*-diphenyl-1,4-phenylenediamine (AA). Steady-state and flash experiments have shown that the reaction takes place adiabatically in the triplet manifold. Two photons are required for the reaction. A triplet energy transfer process prevents the intermediate photoproduct *N,N'*-dimethyl-3-anilino-carbazole (AC) from being accumulated in larger concentrations.

The oxidative photocyclization of diphenylamines yields carbazoles as final products.² This reaction has been applied to synthesize a number of carbazole derivatives and related compounds (for recent reviews see ref 3). The reaction proceeds in many cases adiabatically in the triplet manifold^{3,4} via an unstable zwitterionic dihydrocarbazole.

Recently it was reported⁵ that *N,N'*-dimethyl-*N,N'*-diphenyl-1,4-phenylenediamine (AA) in air-equilibrated solution is by light



converted into *N,N'*-dimethylindolo[3,2-*b*]carbazole (CC'). From a mechanistic point of view this reaction appeared to be of particular interest because *N,N'*-dimethyl-3-anilino-carbazole (AC), which contains *one* five-membered ring, could *not* be detected in the reaction mixture⁵ even at the beginning of the reaction. One would expect that a photostationary concentration of AC accumulates after a certain illumination period if two photons are required (eq 1) for the formation of CC', otherwise a more com-

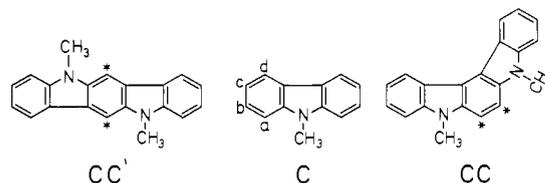


plicated mechanism, eventually including a thermal ring closure, had to be considered.

In this paper we wish to present experimental evidence for a two-photon autosensitization mechanism according to which AC can accumulate in very small concentrations only. Thereby, light energy absorbed by AA is effectively transferred to AC, which subsequently converts into the hitherto unknown final product *N,N'*-dimethylindolo[2,3-*c*]carbazole (CC). The latter reaction is highly regioselective. Detectable amounts of the isomer CC' are not formed.

Results

Steady-State Experiments. Spectra and Product Analysis. In Figure 1 the absorption spectrum of AA in methylcyclohexane (MCH) before (dashed line) and after illumination (solid line) is depicted. In Figure 2 the absorption spectrum of the purified photoproduct (solid line) is compared with an authentic sample of CC'. Clearly, both spectra exhibit the typical, structured bands



of carbazoles but they are by not means identical. Comparing the NMR spectra of CC' with the photoproduct leaves no doubt that the indolocarbazole CC (and not CC', as proposed in ref 5) is formed from AA in oxygen-containing solutions. If one regards *N*-methylcarbazole (C) as indolo-substituted benzene the chemical shift of the 4 protons with respect to benzene ($\delta = 7.26$ ppm) is as follows: $a = 0.16$; $b = 0.24$; $c = -0.01$; $d = 0.89$ ppm. The chemical shift of the two (equivalent) protons (marked with asterisks) in the central benzene rings of CC' and CC is then expected to be as follows: CC', $7.26 + 0.16 + 0.89 = 8.31$ (found, 8.31) ppm and for CC, $7.26 + 0.16 + 0.24 = 7.66$ (found, 7.85) ppm. The very close agreement between the estimated and found value in the case of CC' is, of course, fortuitous, but the expected and observed difference between the two central protons of CC' and CC is without doubt significant and shows that it is correct to assign to the photoproduct the angular structure. In degassed solutions an unstructured UV spectrum ($\lambda_{max} = 330$ nm) appears after illumination of AA. We could not identify the photoproduct(s) formed under anaerobic conditions, because it proved to be impossible to isolate the products by means of GC and HPLC.

The formation of CC as a function of illumination time can be monitored (cf. Figure 1) by measuring the increase in optical density, $E(401)$, at the first absorption peak of CC at 401 nm. If only one photon were required to convert AA into CC and if no slow thermal reaction is involved, $E(401)$ should increase proportionally with time. This is, however, not the case as can be seen from the results given in Figure 3. Only after a certain induction period (about 7 min in Figure 3) formation of CC starts noticeably and increases linearly with time after about 40 min. Leaving the solution after 5 min illumination time for several hours in the dark does not change the absorption spectrum, i.e., the possibility of a slow dark reaction can be excluded. It was logical to assume that during the induction period the anilino-carbazole AC is formed and that a second photon is required to convert AC

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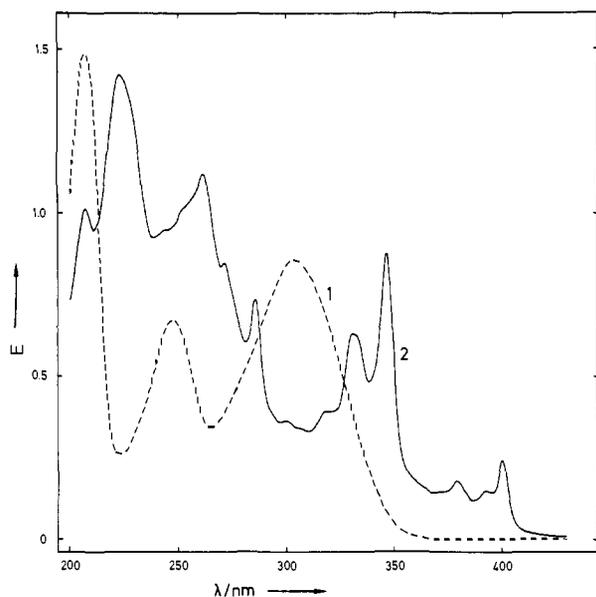


Figure 1. Absorption spectra in MCH, flushed before and during illumination with a gas mixture of 2% O₂ in N₂ ($\sim 2 \times 10^{-4}$ M dissolved oxygen) at 293 K. (1) 4.41×10^{-5} M *N,N'*-dimethyl-*N,N'*-diphenyl-1,4-phenylenediamine (AA); (2) reaction mixture obtained after illumination of 1 with a medium-pressure mercury lamp.

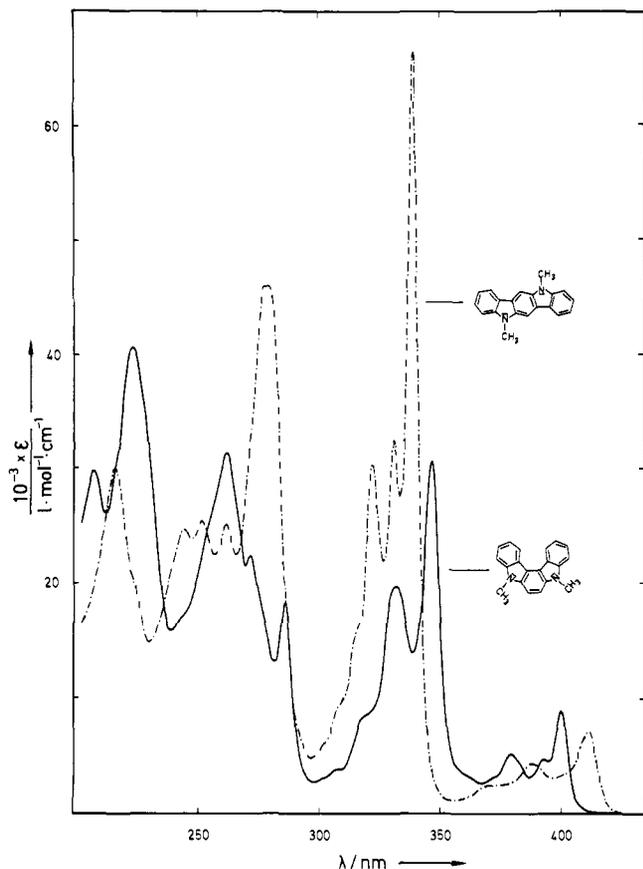


Figure 2. Absorption spectra of *N,N'*-dimethylindolo[2,3-*c*]carbazole (CC) (solid line) and *N,N'*-dimethylindolo[3,2-*b*]carbazole (CC') (dashed line) in MCH at 293 K.

into CC. It was indeed possible to isolate a small amount of AC from a solution of AA that was illuminated until traces of CC appeared in the reaction mixture. The structure of AC was determined by means of NMR and mass spectroscopy. If a solution of AC is illuminated (cf. Figure 4), $E(401)$ increases, as expected, linearly with time without induction period. We therefore conclude that CC is formed in two steps. The spectrum of AC and its photoconversion into CC (both are new compounds)

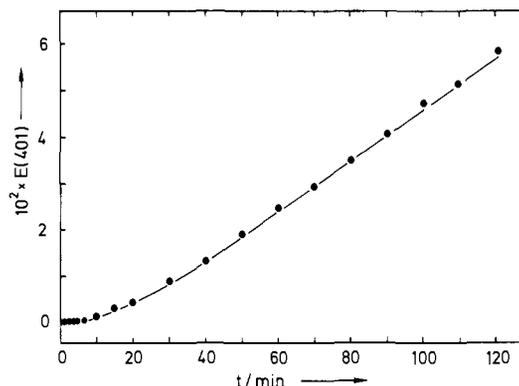


Figure 3. Change of optical density, $E(401)$, at 401 nm as a function of illumination time, t . A solution of 3×10^{-5} M AA in MCH was monochromatically illuminated with 313-nm light at 293 K. The solution was flushed with a gas mixture of 2% O₂ in N₂ (see text).

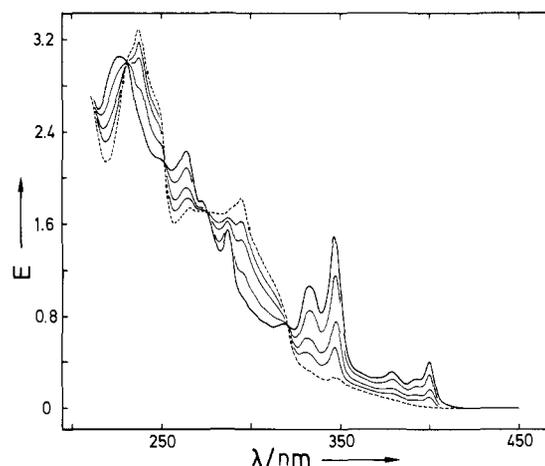


Figure 4. Absorption spectrum of a 7.2×10^{-5} M solution of *N,N'*-dimethyl-3-anilino-carbazole (AC) in MCH (flushed with 5% O₂ in N₂) at 293 K before (dashed line) and after (solid lines) illumination with 313-nm light for 3, 6, 12, and 18 min. (The proportionality between CC formation and illumination time was determined more accurately in separate experiments with smaller conversions.)

is shown in Figure 4. Due to the 3-anilino substituent the characteristic carbazole structure is much less pronounced in the UV spectrum of AC. A similar broadening of the absorption bands in the long-wavelength region is observed if, for instance, in *N*-methylcarbazole the 3- and 5-positions are substituted by a dimethylamino group. According to eq 1 one would expect that the induction period becomes longer if the optical density of the starting material AA is increased. Much to our surprise we did not find such a dependence. We illuminated, for instance, two solutions, 1 and 2, of AA with the optical densities $E_1(313) = 0.46$ and $E_2(313) = 4.58$ monochromatically with 313-nm light under identical conditions and monitored the formation of CC at 401 nm as described above. Conversion was kept low, $E(401)$ ranging from about 10^{-3} to 10^{-2} . Within this range the ratio of optical densities in solution 1 and 2, $R = E_1(401)/E_2(401)$, remained constant ($R = 0.7$) after different illumination times. This means that the evolved CC concentration depends only on the number of light quanta absorbed. (In solution 1 about 65% of the 313-nm light was absorbed, in solution 2 practically 100%.)

From flash experiments (see below) it soon became clear that the photoconversion of AA into CC is sensitized by the intermediate product AC. Thereby, the actinic light is all the time mainly absorbed by AA, but its energy is in increasing proportion transferred to AC, which then converts into CC. Therefore, only small steady-state concentrations of AC can accumulate in the reaction mixture.

The Relation between Oxygen Content and Quantum Yield. The formation of AC from AA and of CC from AC takes place in the triplet manifold, as we shall show below. Since both carba-

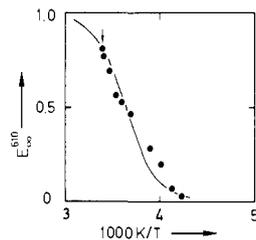


Figure 8. Quantum yield of ^1HAC formation, ϕ_{HAC} , as function of temperature. Dots, end-absorption of ^1HAC monitored at 650 nm (E_{∞}^{650}); solid line, ϕ_{HAC} calculated with eq 2. At one temperature (arrow) the calculated value was fitted to the corresponding experimental point.

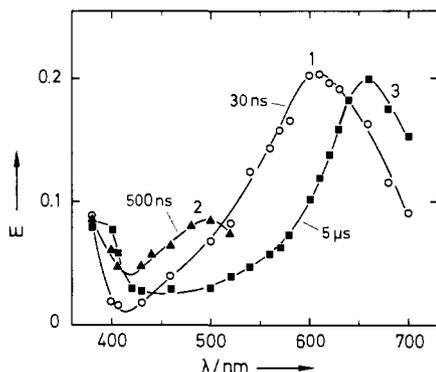


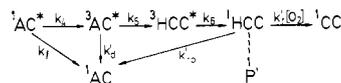
Figure 9. Transient absorption spectra obtained on flashing a 5×10^{-5} M degassed solution of AC in MCH at 278 K with 308-nm light of an exciplex laser. Optical path length of the monitoring light, 20 mm; (1) absorption spectra of $^3\text{AC}^*$; (2) $^3\text{HCC}^*$; (3) ^1HCC ; taken 30 ns, 500 ns, and 5 μs , respectively, after flash excitation.

multate. But by determining the temperature dependence of the quantum yield, $\phi_{\text{HAC}}(T)$, with which the long-lived transient ^1HAC is formed one can at least show that $^3\text{AA}^*$ is a precursor of ^1HAC . Since ϕ_1 was found to be temperature independent, $\phi_{\text{HAC}}(T)$ is according to Scheme I

$$\phi_{\text{HAC}}(T) = \phi_1 k_2(T) \tau_1(T) \quad (\tau_1 = 1/(k_d + k_2)) \quad (2)$$

and proportional to the end-absorption, $E_{\infty}^{650}(T)$, of decay curves monitored at 650 nm. This end-absorption is reached within about 30 μs , when the conversion of $^3\text{AA}^*$ into ^1HAC is finished, and persists for several milliseconds ($\tau_{\text{HAC}} = 55$ ms at 298 K). Its

Scheme II



decay during 30 μs is therefore negligible. The agreement between the drastic drop of $E_{\infty}^{650}(T)$ with decreasing temperature and the relative quantum yield $\phi_{\text{HAC}}(T)$ calculated (eq 2) from the rate data in Figure 7 in the same temperature range is good (Figure 8). It proves that $^3\text{AA}^*$ is indeed a precursor of ^1HAC .

In the presence of oxygen ^1HAC is oxidized ($k_7[\text{O}_2]$) to the stable product AC. In degassed solutions ^1HAC reverts under ring opening with the rate constant $k_{\tau_0} = 1.4 \times 10^{10} \exp(-50/RT)$ s^{-1} back to AA; at lower temperatures this reaction becomes very slow and formation of unidentified products (P in Scheme I) predominates. To determine $k_{\tau_0}(T)$ the intensity of the monitoring light has to be very low in order to avoid photochemical ring opening.^{4c}

***N,N'*-Dimethyl-3-anilino-carbazole (AC).** The photoreaction of the anilino-carbazole AC is kinetically quite similar to AA, but in contrast to AA the entire reaction sequence can be followed step by step (Scheme II).

In flash experiments one finds a short-lived transient in the nanosecond region absorbing with $\lambda_{\text{max}} = 610$ nm, one in the microsecond region ($\lambda_{\text{max}} = 500$ nm), and a third one in the millisecond region ($\lambda_{\text{max}} = 650$ nm). The absorption spectra of the three transients are shown in Figure 9. We assign the short-lived transient to the triplet state, $^3\text{AC}^*$, of the anilino-carbazole, AC, because it is formed (cf. Figure 10b) at the same rate (monitored at 620 nm) as that with which the fluorescence of ^1AC decays ($1/\tau_f = 8 \times 10^7$ s^{-1} ; Figure 10a) and because it is quenched by oxygen. The yield of its formation, ϕ_1 , is constant between 300 and 150 K. Similar to $^3\text{AA}^*$ (cf. Figure 7) two processes ($k'_d = 3 \times 10^5 \exp(-7/RT)$ s^{-1} and $k_5 = 10^{14} \exp(-41/RT)$ s^{-1}) deactivate this triplet state. Again, the frequency factors of the two rate constants (normal triplet decay, k'_d , and adiabatic product formation in the triplet manifold, k_5) are drastically different. In contrast to AA, the intermediate formation of a dihydrocarbazole, HCC, in its triplet state, $^3\text{HCC}^*$ ($\lambda_{\text{max}} =$

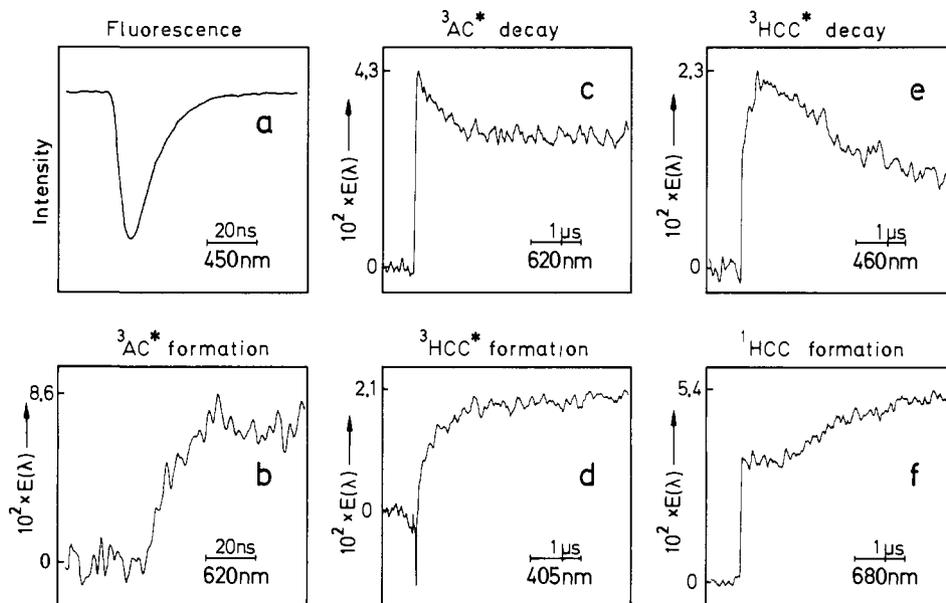
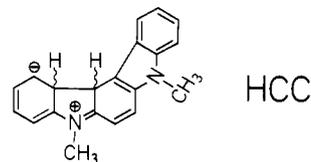


Figure 10. Transient recorder traces after flashing a 5×10^{-5} M degassed solution of AC in MCH at 278 K with 308-nm light of an exciplex laser. Vertical scale: fluorescence intensity in arbitrary units or absorbance, $E(\lambda)$. Monitoring wavelength, $\lambda(\text{nm})$ and time scale as indicated.

500 nm), can be observed in the case of AC by monitoring its buildup at 405 nm (Figure 10d) where the precursor, $^3\text{AC}^*$, has an absorption minimum (cf. Figure 9). It occurs with the same rate as the decay of $^3\text{AC}^*$, monitored at 620 nm (Figure 10c). The decay of $^3\text{HCC}^*$ into its singlet ground state (k_6), ^1HCC , is best observable at 460 nm (Figure 10e), the buildup of ^1HCC ($\lambda_{\text{max}} = 650$ nm) at 680 nm (Figure 10f). The Arrhenius parameters of $k_6 = 6 \times 10^9 \exp(-20/RT) \text{ s}^{-1}$ were determined by measuring the buildup of ^1HCC between 298 and 240 K in MCH-isopentane (1:8 by volume). Above 250 K the dihydrocarbazole ^1HCC decays in degassed solution mainly by ring opening with $k'_{\text{ro}} = 1.5 \times 10^{10} \exp(-48/RT) \text{ s}^{-1}$, below 250 K it slowly degrades into unidentified products (P' in Scheme II). Again, the monitoring light level has to be kept very low to avoid light-induced ring opening.^{4c}

Quenching Experiments. The reciprocal lifetime of the amine triplet state, $^3\text{AA}^*$ is at 295 K $1/\tau_t = (k_d + k_2) = 3.6 \times 10^5 \text{ s}^{-1}$. Addition of AC to a solution of AA shortens the lifetime due to triplet energy transfer:

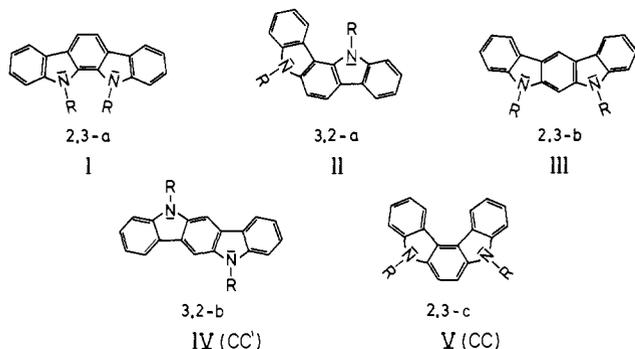


In order to determine the quenching constant k_s , we added to a degassed solution of 2×10^{-4} M AA in MCH 1.04×10^{-4} M AC and excited the sample with 337-nm light of a nitrogen laser. Most of the exciting flash light is absorbed by AA under these conditions. The decay constant of the quenched triplet state $^3\text{AA}^*$ (monitored at 670 nm) is $k_{\text{exp}} = 1/\tau_t + k_s[\text{AC}] = 1.3 \times 10^6 \text{ s}^{-1}$, and the quenching constant becomes $k_s = 9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, which is close to a diffusion-controlled reaction in MCH.

Discussion

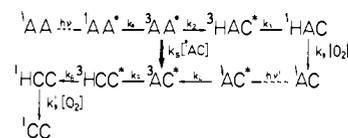
Two aspects of the photoreaction described in this paper are of particular interest, namely the regioselectivity of the second ring-closure reaction $\text{AC} \rightarrow \text{CC}$ and the "autosensitized" triplet energy transfer process (eq 3).

Of the five isomeric indolocarbazoles four (I–IV with R = H



or simple derivatives thereof) have been synthesized thermochemically. The angular isomer V that we obtained photochemically from AA via AC as the sole product is to our knowledge not yet described in the literature. Apparently, the electron distribution in the excited triplet state of AC leads to this remarkable regioselectivity of the ring-closure reaction. We will discuss this aspect elsewhere, including other diphenylamines, where similar observations have been made. It is interesting to note that the linear isomer IV was prepared⁷ from *N,N'*-diphenyl-1,4-phenylenediamine (i.e., AA with NH instead of NCH_3 groups) in the gas phase at 560 °C on a platinum-magnesium oxide catalyst, and the authors state expressively that they did not find the angular isomer V in the reaction mixture. Other attempts⁸ to synthesize V by Fischer indolization also met with failure. If one keeps in mind that an optimized oxygen concentration level (cf. Figure 5) should be maintained during the photoreaction, it is not difficult to prepare V (with R = CH_3) in gram amounts photochemically. Problems may arise if R = H, because in the case of diphenylamine we found radical reactions,

Scheme III



initiated by hydrogen abstraction from the NH group, when the oxygen content of the solution was kept low. These side reactions led to a very complex mixture of byproducts.

The results of our kinetic experiments are summarized in Scheme III which is a combination of Schemes I and II, linked by the autosensitization reaction with rate constant $k_s[\text{AC}]$ and simplified by neglecting competitive steps [k_f , k_d , k_{ro} , etc.]. Both compounds AA and AC react photochemically like *N*-methyl-diphenylamine^{4a} (MDPA), i.e., the primary photoproducts HAC and HCC are formed *adiabatically* in the triplet manifold. Since the triplet states $^3\text{AA}^*$ and $^3\text{AC}^*$ are relatively long lived, the oxygen concentration that gives the highest CC quantum yield is rather low (5×10^{-5} M, cf. Figure 5). In the case of MDPA the triplet lifetime is much shorter and the optimal oxygen concentration^{4b} is correspondingly higher (4×10^{-4} M).

From Scheme III it becomes clear that the induction period shown in Figure 3 is in concentrated solutions mainly determined by the autosensitization process $k_s[\text{AC}]$, because very little light will be absorbed by AC itself. When the concentration of the energy acceptor has accumulated to the value $\text{AC} = 3 \times 10^{-5}$ M, the rate constants of the two competing processes $k_2 = 2.4 \times 10^5 \text{ s}^{-1}$ and $k_s[\text{AC}] = 2.7 \times 10^5 \text{ s}^{-1}$ (in MCH at 293 K) are about equal, and the photostationary AC concentration will therefore be in the range of 10^{-4} M.

Experimental Section

Materials. *N,N'*-Dimethyl-*N,N'*-diphenyl-1,4-phenylenediamine (AA). *N,N'*-Diphenyl-1,4-phenylenediamine (14 g, 0.05 mol) was dissolved in orthoformic acid trimethyl ester (20 g, 0.19 mol) and stirred for 30 min at 100 °C; within 1 h the temperature was raised to 180 °C and kept for 30 min. Methanol formed was distilled off with a Vigreux column, last traces were removed under vacuum. After addition of 40 mL of KOH (15%) the sample was refluxed for 4 h and the warm reaction mixture extracted with CHCl_3 . The extract was chromatographed (Al_2O_3 , cyclohexane-diisopropyl ether 1:1), several times recrystallized from ethanol (under a nitrogen atmosphere in the dark), vacuum sublimed and finally zone melted (30 cycles). Yield 700 mg (5%) *N,N'*-dimethyl-*N,N'*-1,4-phenylenediamine; white crystals; mp 158.3–158.7 °C; UV_{max} (log ϵ) in methylcyclohexane 304 (4.27), 248 (4.18) nm; fluorescence_{max} in methylcyclohexane 398 nm; NMR ($\text{Me}_2\text{SO}-d_6$) 7.22 (4 H, t), 6.99 (4 H, s), 6.91 (4 H, d), 6.85 (2 H, t), 3.24 (6 H, s).

N,N'-Dimethyl-3-anilino-carbazole (AC). AA (300 mg, 0.001 mol) was dissolved in 1 L of methylcyclohexane, the solution was placed in a quartz vessel, flushed with a mixture of N_2/O_2 (98:2) 15 min prior and during 90-min illumination in a Rayonet-Photoreactor with 10 16-RPR-300 nm lamps. After 90-min illumination formation of CC just started (UV control). After evaporation of the solvent the reaction mixture was chromatographed on Al_2O_3 with cyclohexane-ether 1:1. The yield (after recrystallization from petroleum ether) was 36 mg (12%) of *N,N'*-dimethyl-3-anilino-carbazole (AC); white crystals; mp 118.9–119.6 °C; UV_{max} (log ϵ) in methylcyclohexane 348 (3.49), 295 (4.32), 266 (4.27), 237 (4.41) nm; fluorescence_{max} in methylcyclohexane 405, 423 nm; NMR ($\text{Me}_2\text{SO}-d_6$) 8.1–6.7 (12 H, m), 3.85 (3 H, s), 3.33 (3 H, s).

N,N'-Dimethylindolo[2,3-c]carbazole (CC). AA (300 mg, 0.001 mol) was under the same conditions as above (AC) illuminated for 5 h. The yield (after recrystallization from toluene) was 100 mg (30%) of *N,N'*-dimethylindolo[2,3-c]carbazole (CC); white crystals; mp 257.6–258.2 °C; UV_{max} (log ϵ) in methylcyclohexane 401 (3.93), 393 (3.67), 379 (3.73), 347 (4.49), 332 (4.29), 308 (3.59), 286 (4.26), 272 (4.35), 262 (4.50), 223 (4.61) nm; NMR ($\text{Me}_2\text{SO}-d_6$) 8.78 (2 H, doublet), 7.84 (2 H, singlet), 7.71 (2 H, doublet), 7.53 (2 H, triplet), 7.36 (2 H, triplet), 4.02 (6 H, singlet).

N,N'-Dimethylindolo[3,2-b]carbazole (CC') was prepared according to ref 9.

Flash Photolysis, Spectra, Irradiation, Solvents. Sample preparation and recording of steady-state and flash spectra has been described in ref

(7) Grotta, H. M.; Riggle, J. C.; Bearnse, A. W. *J. Org. Chem.* **1961**, *26*, 1509–1511.

(8) Robinson, B. *J. Chem. Soc.* **1963**, 3097–99.

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4a and 4c. NMR spectra were recorded with a Bruker Spektrospin 270-MHz spectrometer.

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Reactions of Dihydrido(bicarbonato)bis(triisopropylphosphine)rhodium(III) with Alkynes. Formation of $\text{Rh}_2\text{H}_2(\text{O}_2\text{CO})(\text{PhC}\equiv\text{CPh})(\text{P}(i\text{-Pr})_3)_3$ and the Stereoselective Hydrogenation of Alkynes to Trans Olefins

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Abstract: A reaction of $\text{RhH}_2(\text{O}_2\text{COH})(\text{P}(i\text{-Pr})_3)_2$ (**1**) with $\text{PhC}\equiv\text{CPh}$ has been found to give *trans*-stilbene and a novel binuclear rhodium complex $\text{Rh}_2\text{H}_2(\text{O}_2\text{CO})(\text{PhC}\equiv\text{CPh})(\text{P}(i\text{-Pr})_3)_3$ (**2**). A similar reaction with $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$ results both in H_2 evolution and half-hydrogenation, while with $\text{F}_3\text{C}\equiv\text{CCF}_3$ only H_2 evolution is observed. Compound **1** catalyzes the stereoselective half-hydrogenation of alkynes to *trans* olefins. Complex **2** crystallizes in the monoclinic space group $C_{2h}^5-P2_1/c$, with four formula units in a cell of dimensions $a = 17.158$ (4) Å, $b = 23.916$ (3) Å, $c = 11.255$ (3) Å, $\beta = 103.3$ (1)°, and $V = 4494$ Å³ ($t \approx -160$ °C). In the solid state **2** consists of a distorted octahedral Rh(III) center and a distorted square-planar Rh(I) center bridged by a bis-bidentate carbonato group.

Cis dihydrides of transition metals have received considerable attention as catalysts for the hydrogenation of unsaturated organic molecules. The reaction proceeds through insertion of the unsaturated molecule into the M-H bond.² An alternative reaction of cis dihydrides with π -acids is reductive elimination to produce dihydrogen. Recently we have observed both types of reactions for the cis-dihydrido carbonato and formato compounds RhH_2XL_2 ($X = \text{O}_2\text{COH}, \text{O}_2\text{CH}; L = \text{P}(i\text{-Pr})_3, \text{P}(\text{C}-\text{C}_6\text{H}_{11})_3$).³ Thus, reaction with CO_2 under ambient conditions leads readily to reduction of the substrate, while reaction with CO results in dihydrogen evolution. Both reactions afford the carbonyl compounds *trans*- $\text{Rh}(\eta^2\text{-O}_2\text{COH})(\text{CO})\text{L}_2$ and *trans*- $\text{Rh}(\eta^2\text{-O}_2\text{CH})(\text{CO})\text{L}_2$, respectively. A facile dihydrogen evolution is also observed on treatment of the cationic cis-dihydrido compounds $[\text{RhH}_2(\text{S})_2\text{L}_2]^+$ ($\text{S} = \text{solvent}, L = \text{phosphine}$) with CO and *t*-BuNC.^{4,5} The square-planar cis-dihydrido compound $\text{PtH}_2(\text{diphos})$ ($\text{diphos} = (t\text{-Bu})_2\text{P}(\text{CH}_2)_2\text{P}(t\text{-Bu})_2$) reacts with olefins carrying electron-withdrawing substituents, e.g., acrylonitrile and maleic anhydride, to afford the compounds $\text{Pt}(\text{olefin})(\text{diphos})$ with evolution of H_2 .⁶ Recent MO calculations⁷ are consistent with this facile reductive

elimination of H_2 . By contrast, the compound $\text{PtH}_2(\text{diphos})$ is inert toward cyclohexene under ambient conditions, while under forcing conditions (100 °C, 80 Kg/cm² of H_2) it catalyzes the hydrogenation to give cyclohexane.⁶ Apparently the reaction of cis-dihydrido complexes with π -acid is sensitive to the π -acidity of the substrate.

In this paper we examine the types of reactions that occur between the cis-dihydrido $\text{RhH}_2(\eta^2\text{-O}_2\text{COH})(\text{P}(i\text{-Pr})_3)_2$ (**1**)³ and the alkynes $\text{PhC}\equiv\text{CPh}$, $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$, and $\text{F}_3\text{CC}\equiv\text{CCF}_3$. The reaction with $\text{PhC}\equiv\text{CPh}$ affords the half-hydrogenation product *trans*-stilbene, together with a new binuclear dihydrido carbonato diphenylacetylene compound characterized by diffraction and spectroscopic methods to be $\text{Rh}_2\text{H}_2(\text{O}_2\text{CO})(\text{PhC}\equiv\text{CPh})(\text{P}(i\text{-Pr})_3)_3$ (**2**). A similar reaction with $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$ results both in H_2 evolution and hydrogenation to give dimethyl fumarate. In contrast, with the stronger π -acid $\text{F}_3\text{CC}\equiv\text{CCF}_3$ only H_2 evolution is observed. As the stereospecific half-hydrogenation of alkynes with homogeneous catalysts to afford *trans* olefins is rare,^{8,9} we also describe our studies of the hydrogenation of $\text{PhC}\equiv\text{CPh}$ as catalyzed by **1** and **2**.

Results and Discussion

Reaction of $\text{RhH}_2(\eta^2\text{-O}_2\text{COH})(\text{P}(i\text{-Pr})_3)_2$ with $\text{PhC}\equiv\text{CPh}$. Reaction of the colorless compound $\text{RhH}_2(\eta^2\text{-O}_2\text{COH})(\text{P}(i\text{-Pr})_3)_2$ (**1**)³ with an excess (3 molar equiv) of $\text{PhC}\equiv\text{CPh}$ in toluene occurs

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