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The Photochemical Formation of Dihydrocarbazoles from Diphenylamines and Their Thermal Rearrangement and Disproportionation Reactions

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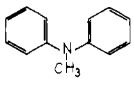
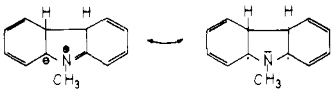
Abstract: *N*-Methyldiphenylamine, A, is in oxygen-free solution converted by light into *N*-methylcarbazole, C, and *N*-methyltetrahydrocarbazole, THC, via a disproportionation reaction. The precursor of C and THC is an unstable 4a,4b-dihydrocarbazole, DHC. Its decay was studied by means of flash and steady state illumination experiments at different temperatures. The primary photoproduct of the A derivative *N*-methyl-2,4,6-trimethyldiphenylamine, TMA, is a 4a-methyl-4b-hydrocarbazole, MDHC. Like DHC it is unstable but rearranges into stable methylhydrocarbazoles, MDHC′. It does not disproportionate like DHC. The photoproducts formed from A, deuterated A, and TMA were analyzed by means of NMR and mass spectrometry.

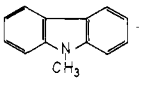
The photocyclization reaction of *N*-methyldiphenylamine, A, to *N*-methylcarbazole, C, has been studied in recent years in several laboratories.[2] Since under certain conditions both the quantum and the chemical yields of this reaction are rather high it has been utilized for the synthesis of a number of carbazoles[3] and indoles[4] as well as for the synthesis of furan[5] and thiophene[6] derivatives. While it is important for preparative purposes to understand the interdependence of oxygen concentration and yield, the study of the reaction sequence in oxygen-free solutions is more interesting from a mechanistic point of view.



A

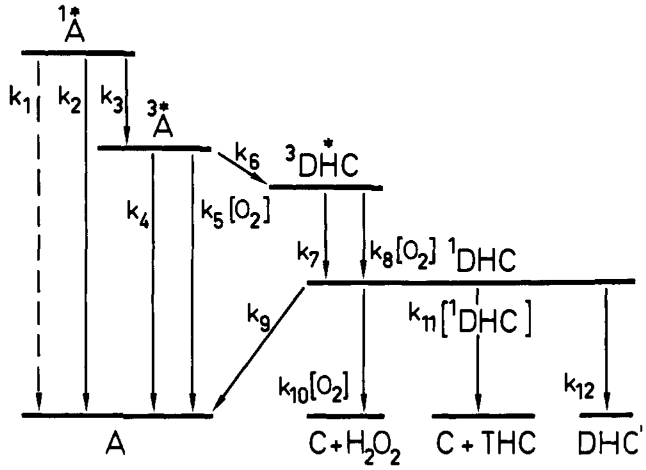


DHC



C

Scheme I



In Scheme I the rather complex reaction mechanism is summarized. It has been elucidated mainly by means of flash photolytic experiments in the nano- and microsecond range[2c,d,k,l,m,n] and is discussed in detail in ref 2m. After light absorption and highly efficient intersystem crossing from the first excited singlet state ${}^1A^*$ to the first excited triplet state ${}^3A^*$ of the amine A, ring closure occurs adiabatically and, presumably, conrotatorily[7] to the primary photoproduct 4a,4b-dihydro-*N*-methylcarbazole, DHC, in its excited triplet state, ${}^3DHC^*$. This triplet state decays rapidly to the singlet ground state, ${}^1DHC$, which has two absorption maxima at 610 nm ($\epsilon_{610} = 2 \times 10^4$ M^{-1} cm^{-1}) and 370 nm ($\epsilon_{370} = 5 \times 10^3$ M^{-1} cm^{-1}).[2m] Because of this long wavelength absorption maximum we proposed[2c,m] the DHC structure for which two resonance forms are given above. Its decay rate can be measured conveniently in microsecond flash experiments by using 610 nm as the monitoring wavelength. Above 250 K the decay is strictly first order and strongly temperature dependent. In an earlier paper[2m] we published an Arrhenius plot from DHC decay constants which were first order all the way between 335 and 130 K with a temperature-independent part (rate constant $k = 1.3$ s^{-1}) between 240 and 130 K (open circles in Figure 1). It turned out that this temperature-independent process is due to a light-induced ring-opening reaction DHC* → A caused by the monitoring light of the flash apparatus. The quantum yield of this reaction is rather high and in the low-temperature region very low monitoring light levels have to be used to make the rate of

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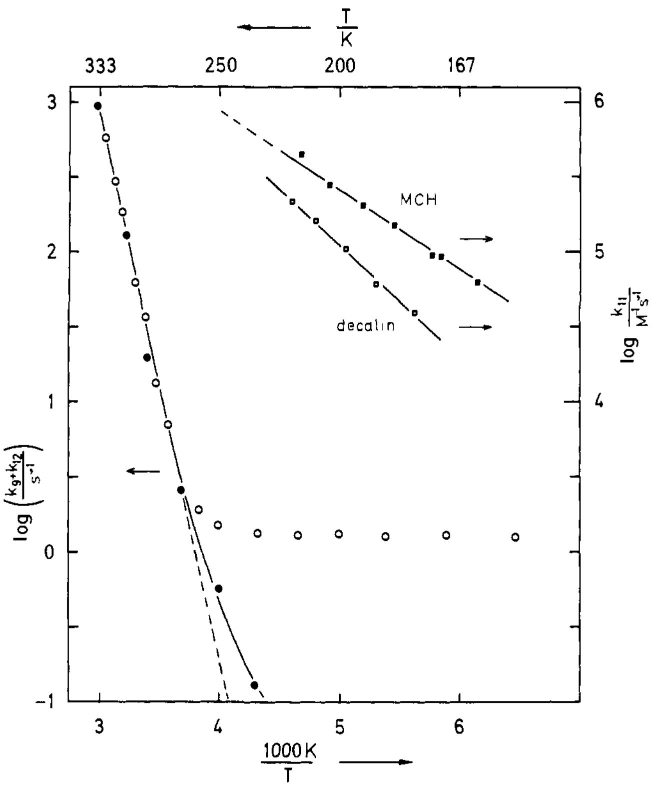

Figure 1. Arrhenius plot of the decay of DHC monitored at 610 nm in degassed MCH and decalin. Left hand scale: First order rate constants. Full monitoring light intensity (○): 100 W iodine-quartz lamp, 450 nm cut-off filter, focal length of collimating lens 10 cm, aperature 0.5 cm; reduced light intensity (●): 0.01% of full intensity, attenuated by 610 nm interference and neutral density filters. Solvent: MCH. Right hand scale: Second order rate constants measured with attenuated monitoring light intensity. Solvents: MCH (■) and decalin (□). The rate constants k_{11} were calculated using the experimentally determined rate constants $k_{exp} = k_{11}/\epsilon_{610} \cdot d$ [s^{-1}], $\epsilon_{610} = 2 \times 10^4$ M^{-1} cm^{-1}, and $d = 10$ cm. The determination of ϵ_{610} was reported in ref 2m.

this photoreaction negligibly small compared with the thermal reactions. It is easy to show[2m] that the thermal ring opening, k_9, is the first-order process because in degassed solution the quantum yield of carbazole and tetrahydrocarbazole (THC) formation by disproportionation ($k_{11}[^1DHC]$) increases with decreasing temperatures until it reaches a constant value between 240 and 110 K. At about 240 K k_9 and $k_{11}[^1DHC]$ are equal. Above that temperature k_9 and below $k_{11}[^1DHC]$ predominates. Below 110 K the DHC yield drops rapidly because k_6 has a higher activation energy than k_4 and the "normal" triplet deactivation reaction k_4 becomes the major reaction pathway in this temperature range.

In aerated solutions DHC is dehydrogenated by oxygen to give C and H_2O_2 ($k_{10}[O_2]$). In the absence of oxygen ^{1}DHC rearranges (k_{12}) to some extent into another dihydrocarbazole, DHC′, but mainly it disproportionates[9] (k_{11}[DHC]) into carbazole, C, and tetrahydrocarbazole, THC. It is this reaction branch in Scheme I (k_9, k_{11}, and k_{12}) which we will discuss in this paper in more detail.

Results and Discussion

The rate constants of the DHC decay were determined in flash experiments with low monitoring light intensities between 335 and 160 K. An Arrhenius plot between 335 and 270 K (Figure 1, left-hand scale) yielded a straight line. From its slope an activation energy of 69 kJ/mol was calculated. Below 250 K the decay of DHC is much faster than predicted from the extrapolated Arrhenius plot and the reaction order changes from first order to second order (Figure 1, right-hand scale). The activation energy of the second-order process is 7 kJ/mol in methylcyclohexane (MCH) and 15 kJ/mol in decalin. The deviation of the Arrhenius plot at lower temperatures (last two points at 250 and 233 K in Figure 1, left-hand scale) is presumably due to the rearrangement reaction k_{12}. These two points were calculated from first-order plots of the last part of the decay curves. At the beginning the decay is mixed first and second order. At 250 K, for instance, $k_{11} \approx 10^6$ M^{-1} s^{-1} (dashed line, right-hand scale in Figure 1), the absorbance at time zero is $E_0 = 0.04$ and with $\epsilon_{610} = 2 \times 10^4$ M^{-1} cm^{-1} and $d = 10$ cm the concentration of DHC becomes $c_0 = 2 \times 10^{-7}$ M. Therefore, $k_{11}c_0 = 0.25$ s^{-1} whereas $(k_9 + k_{12}) = 0.56$ s^{-1}, i.e., the half-lives of the two reactions are comparable at the beginning of the decay.

If one illuminates a solution of A in degassed isopentane at 200 K, i.e., at a temperature at which $k_9 < k_{11}$[DHC], the occurrence of side reactions leading to other products besides carbazole becomes quite evident in the absorption spectrum of the reaction mixture which is depicted in Figure 2 together with the spectra of C and A and the transient spectrum of ^{1}DHC. Obviously, at least one other compound with a poorly structured absorption spectrum is formed besides C. (In the presence of oxygen one observes only carbazole formation.)

It is possible to separate C from the byproduct by treating the solution after illumination with concentrated hydrochloric acid. The apparently less basic C remains in the organic solvent layer. Quantitative measurements showed[9] that 50% of a given amount of amine is converted into C and 50% into a second substance, the mass spectrum of which is very similar to that of C but with a 4 mass units higher parent peak (185). Furthermore, this second substance is completely converted into C during the passage through a gas-chromatographic column. These facts reveal a very close relationship between the two products. We therefore conclude that the byproduct is a tetrahydrocarbazole, THC.

Since 1 mol of C and 1 mol of THC are formed from 2 mol of A and since the primary photoproduct is a dihydrocarbazole, DHC, it is obvious that the formation of C and THC is a disproportionation reaction. This was also demonstrated[9] by the lack of the formation of C and THC on irradiation in highly viscous solvents (decalin at 123 K, paraffin oil at 220 K) where second-order reactions are suppressed to a great extent. Under these conditions A was converted to a product which was not investigated further. Presumably, a rearranged dihydrocarbazole, DHC′, is formed by reaction k_{12}. In agreement with the disproportionation mechanism is the change of the reaction order from first to second order in fluid solution in the low-temperature region where k_{11}[DHC] predominates over $k_9 + k_{12}$. In Figure 2, curve 4, the short wavelength part of the transient absorption of DHC at 170 K is depicted. At this temperature DHC decays in MCH within about 20 s in a second-order reaction (cf. Figure 1) into stable products, the absorption of which is identical with curve 2 in Figure 2. Therefore, one observes within the two isosbestic points at 334 and 343 nm (cf. Figure 2, curves 2 and 4) immediately after the excitation of the amine a rapid, steplike increase in absorbance due to the formation of DHC, followed by a slow growing-in. The latter is caused by the formation of the final products and it has the same second order rate constant as the decrease observed at long wavelengths, e.g., 610 nm (cf. Figure 1). This agreement in rate constants for decay and buildup proves that the final products originate from DHC. Accordingly, at the isosbestic points the growing-in is not observed because the decaying DHC and the emerging final products have the same absorbance at these two wavelengths.

In order to investigate the disproportionation reaction further we carried out some comparative NMR and mass spectrometry experiments with *N*-methyl-2,4,6,2′,4′,6′-hexadeuteriodiphenylamine, A_d, *N*-methyl-2,4,6-trimethyldiphenylamine, TMA, and the parent amine, A. We compared the 270 MHz NMR spectra[11]

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[11] We are greatly indebted to Dr. H. Grell for performing these measurements.

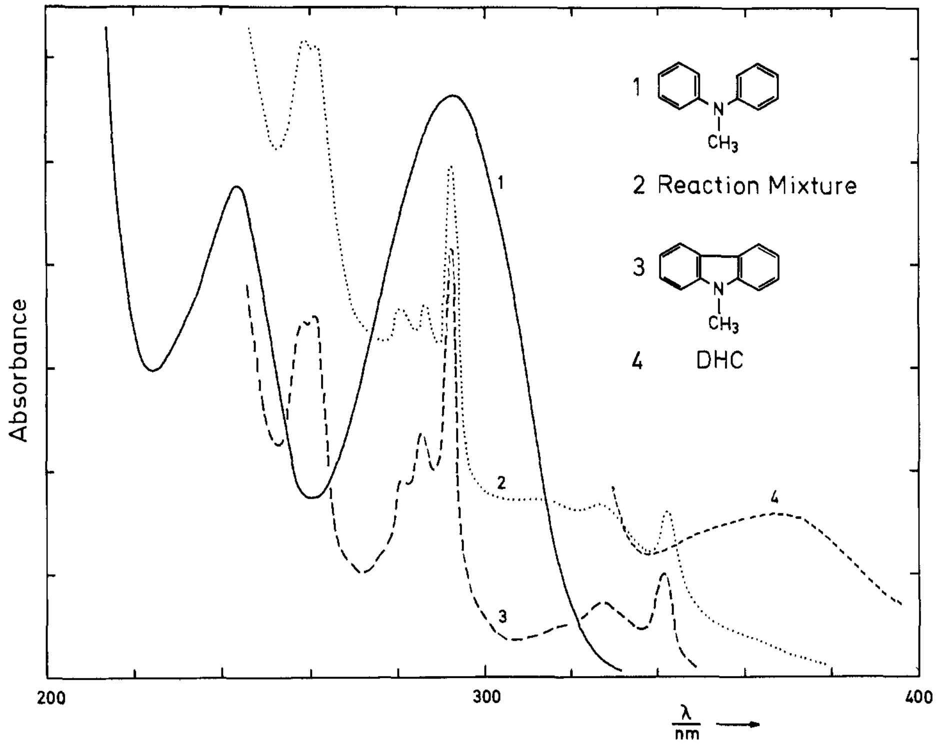
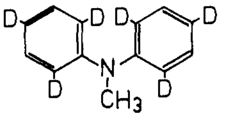
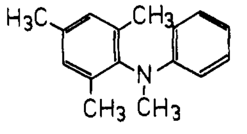


Figure 2. Absorption spectra in degassed methylcyclohexane at 296 K. (1) *N*-Methyldiphenylamine; (2) reaction mixture obtained after illumination of (1) at 200 K and warming to 296 K; (3) *N*-methylcarbazole separated from mixture (2); (4) short wavelength part of the transient spectrum of DHC at 170 K taken from decay curves at time zero. (The main absorption band of DHC has a maximum at 610 nm.)

of C (from an authentic sample) and of a reaction mixture obtained after illumination of A in isopentane at 200 K. As we have shown above the reaction mixture consists of C and THC. Since THC turned out to be a labile substance we did not attempt in this experiment to separate the carbazole from the mixture in order to keep isomerization reactions to a minimum. The assignment of the carbazole signals in Table I is unambiguous and the integral of the *N*-methyl protons, a, was used as standard for the determination of the number of protons from the other signals.



A$_d$



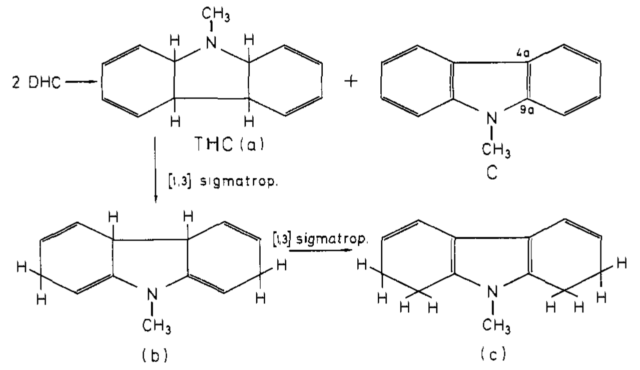
TMA

In the reaction mixture (sections THC and DHC″ of Table I) one finds that besides the *N*-methyl signal, a, of C (δ 3.83) not one but two other *N*-methyl signals, a′ and a″, appear. After the reaction mixture has stood for several hours the integral of signal a″ increases and that of a′ decreases correspondingly. The sum of the integrals a′ and a″ is, however, always equal to the integral of signal a. This fact corroborates our disproportionation mechanism according to which 50% C and 50% THC are formed.

Obviously, THC decomposes with time into another compound. According to the NMR spectrum this compound has to have an aromatic ring (signal f″) which means that THC is thermally dehydrogenated to a dihydrocarbazole DHC″ which is relatively stable and perhaps not identical with DHC′. The structures for THC and DHC″ given in Table I are in agreement with the observed NMR spectra. The coupling of the protons c′–d′, c′–e′, d′–e′, c″–d″, c″–e″, and d″–e″ has been verified experimentally by decoupling experiments.

The appearance of DHC″ in the NMR spectra is not surprising. Dehydrogenation of tetrahydrocarbazoles has been reported in several papers.[10a–c] It is also possible that the THC originally formed rearranges by hydrogen shifting during the illumination time and during removal of the solvent when concentrated solutions for NMR spectra are prepared. It is therefore impossible to determine from the above data which hydrogen atoms are transferred during the disproportionation reaction.

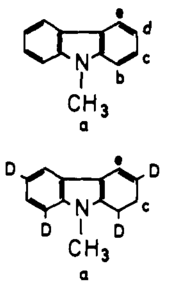
Scheme II



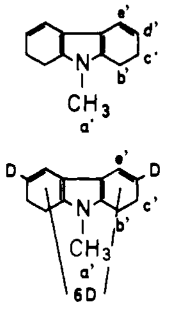
More information in this respect is gained from experiments carried out with the deuterated amine, A$_d$. The temperature dependence of the deuterated and the undeuterated DHC decay and the absolute values of k_{11} are identical.[8] Consequently we observe the same three *N*-methyl signals a, a′, and a″. Furthermore, the carbazole proton signals e (δ 8.15) and c (δ 7.5) have the same chemical shift as those listed in Table I but they appear now as singlets, because they have deuterium atoms as neighbors. The b and d signals are not present, i.e., the positions of the D atoms at the corresponding carbon atoms have not changed during the carbazole formation. Similarly, one observes singlet signals of e′ (δ 6.45) and e″ (δ 6.75), but not of d′ and d″, i.e., the latter positions are occupied by D atoms.

Very important in this context are the molecular weights of the photoproducts which were determined by mass spectrometry. We isolated a carbazole with a parent peak at 185 mass units and observed in the reaction mixture a THC the molecular weight of which was 193. The isolated carbazole has therefore two deuterium atoms less and the THC two deuterium atoms more than A$_d$ (the molecular weight of A$_d$ is 189). Since the positions of the remaining 4 D atoms do not change we have to conclude that two DHC molecules come in contact in such a way that the

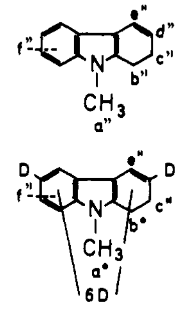
Table I. NMR Data of *N*-Methylcarbazole, C, and of a Reaction Mixture Obtained after Illumination of *N*-Methyldiphenylamine, A, in Degassed Isopentane at 200 K



C



THC



DHC"

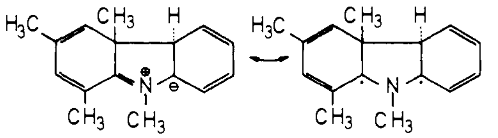
compd	protons	no. of protons^b	shift, δ (ppm)	splitting^c	coupling constant $J_{n,n}$	Hz
C	a	3	3.83	s		
	b	2	7.41	d	b–c	
	c	2	7.51	t	c–d	
	d	2	7.26	t	d–e	
	e	2	8.1	d		
THC^a	a'	3	3.3	s		
	b'	4	2.65	t	b'–c'	9.2
	c'	4	2.4	m	c'–d'	4.2
	d'	2	5.55	2t	d'–e'	9.6
	e'	2	6.54	2t	c'–e'	2.1
DHC"^{a}	a"	3	3.6	s		
	b"	2	2.9	t	b"–c"	9.2
	c"	2	2.55	m	c"–d"	4.2
	d"	1	5.65	2t	d"–e"	9.6
	e"	1	6.75	2t	c"–e"	2.1
	f"	4	7.0–7.7	m		

^{a} Contained in the reaction mixture. ^{b} Based on the three methyl protons a. ^{c} s = singlet, t = triplet, m = multiplet, 2t = doublet splitted into two triplets.

4a,4b-deuterium atoms can be transferred from one of the DHC molecules to the other to give THC(a) and C (Scheme II). The tetrahydrocarbazole THC(a) rearranges further without participation of the 3,4,5,6 positions by two [1,3] sigmatropic hydrogen shifts yielding finally the tetrahydrocarbazole THC(c), the structure of which is in agreement with the observed NMR spectra.

The observed exchange of the deuterium atoms at the 4a,4b-bridge of DHC made the investigation of *N*-methyl-2,4,6-trimethyldiphenylamine, TMA, quite interesting, because in this compound one H atom at that bridge is replaced by a methyl group. (We also investigated briefly *N*-methyl-2,4,6,2',4',6'-hexamethyldiphenylamine,[12] but the absorption spectrum and the photochemistry of this molecule are entirely different from those of the other amines, presumably due to the strong steric interaction between the methyl groups at the two phenyl rings.)

In flash experiments carried out with TMA one observes a ring closure reaction sequence to MDHC which proceeds about 10 times faster than the DHC formation. One can estimate that as a consequence of this the rate constant k_4 in Scheme I becomes comparable with k_6 only at about 50 K and the yield of MDHC (Figure 3b) therefore remains constant between room temperature and 77 K. (For technical reasons we so far have not extended our measurements below this temperature.)



N-methyl-4a-methyl-4b-hydro-1,3-dimethylcarbazole
MDHC

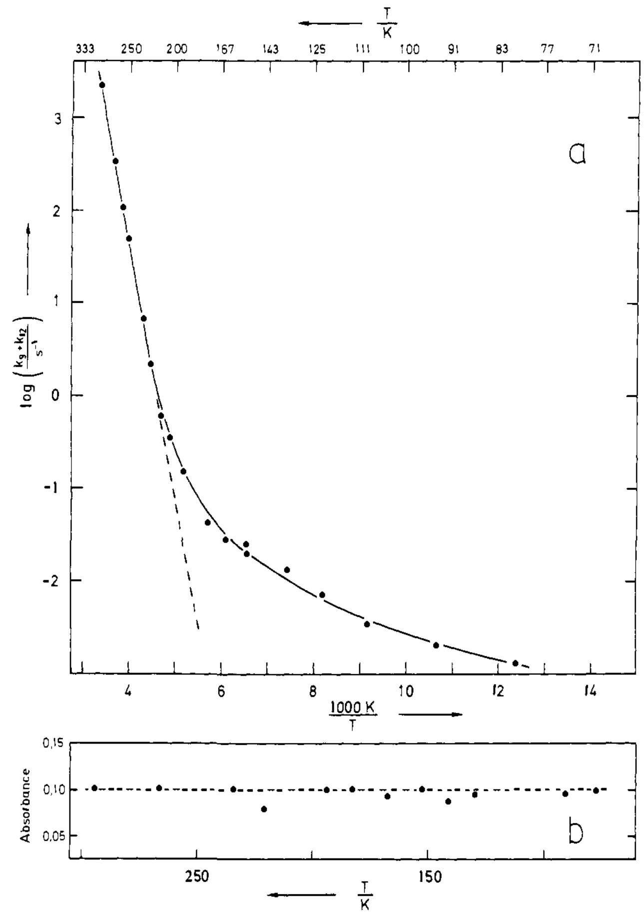


Figure 3. (a) Arrhenius plot of the decay of MDHC in methylcyclohexane-isopentane 20:1, monitored at 620 nm with low light intensity. (b) Absorbance of MDHC at 590 nm at different temperatures shortly after flash excitation and prior to noticeable MDHC decay in methylcyclohexane-isopentane 20:1.

In principle, there is no difference between A and TMA up to the point where DHC or MDHC, respectively, are formed. MDHC has an absorption maximum at 640 nm. In contrast to DHC the decay of MDHC is strictly first order, not only at high temperatures, but over the entire region investigated. At high temperatures its decay is mainly determined by the ring-opening reaction, k_9, which has an activation energy of 54 kJ/mol (Figure 3a). Below 200 K the observed decay of MDHC is faster than predicted (dashed line in Figure 3a) from this activation energy. This is due to the rearrangement reaction k_{12}, MDHC → MDHC', with a temperature-dependent activation energy which becomes increasingly smaller at lower temperatures than that of k_9. If one illuminates degassed solutions of TMA in MCH at 173 K where $k_{12} \gg k_9$, one obtains a reaction mixture of compounds which does not exhibit any structured absorption typical of carbazoles and has a mass spectrum quite similar to that of the amine itself. In particular there is no compound detectable with a molecular weight higher than that of the amine TMA (225). We therefore conclude that MDHC, in contrast to DHC, does not disproportionate. The NMR spectrum of the reaction mixture contains a great number of closely spaced lines. During illumination some of the signals become less intense while others grow, indicating subsequent rearrangements MDHC' → MDHC" occurring during the photoreaction. It was possible to separate three of the isomers by means of preparative gas chromatography. The NMR spectra of these isomers differ only slightly from each other. In the region of the aromatic protons (δ 7–8) we find 4 protons which split into two doublets and two triplets quite similar to the aromatic proton signals in Table I. Therefore, the aromatic ring must contain only

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[12] (a) Hinkel, L. E.; Summers, G. H. R. *J. Chem. Soc.* **1952**, 2813. (b) Thanks are due to M. Kaganowitsch from the Weizmann Institute (Israel) for the synthesis of this compound.

protons and no methyl groups. The exact position of the methyl groups cannot be determined from these experiments but it is safe to assume that during the initial rearrangement reaction (k_{12} in Scheme I) a hydrogen migrates and not a methyl group. This hydrogen shift at low temperatures is one of the most interesting aspects of the photoreactions of A and, especially, TMA. The very small and apparently temperature dependent activation energy (cf. Figure 3a) in the case of TMA indicates that a tunneling process may become important. Steady state experiments designed to isolate the primary rearrangement product and kinetic experiments carried out at temperatures below 77 K with deuterated and undeuterated TMA are in progress.[8] In the case of A, the disproportionation reaction 2DHC $\rightarrow$ C + THC is predominant which makes the determination of k_{12} and the structure analysis of the rearrangement product extremely difficult.

Experimental Section

Materials. *N*-Methyldiphenylamine (Eastman-Kodak, Anal. Grade) was purified by several distillations until the purity was >99.99% (determined by GC).

***N*-Methyl-1,3,5,1′,3′,5′-hexadeuteriodiphenylamine** (Merck, Sharp and Dohme) was used without further purification (isotopic purity 90 atom % D, by MS).

***N*-Methyl-2,4,6-trimethyldiphenylamine.** 2,4,6-Trimethylacetanilide (84.5 g, 0.5 mol) and 264 mL (2.4 mol) of iodobenzene were suspended in 380 mL of dry nitrobenzene and 181 g (1.1 mol) of K_2CO_3 and 3 g of freshly precipitated and washed (dry ether) Cu were added. The mixture was refluxed under stirring for 48 h at 200 °C. The suspension was filtered, with 1.5 L $CHCl_3$ extracted, the solvent evaporated, and the residue chromatographed on Al_2O_3 with cyclohexane–ether 1:1; yield 3.67 g (2.9%) *N*-acetyl-2,4,6-trimethyldiphenylamine; mp 109.1 °C; IR (KBr) 1670 cm^{-1} (CO). Hydrolysis with KOH in triethylene glycol (24 h under reflux) yielded 2.6 g (70%) of 2,4,6-trimethyldiphenylamine which was recrystallized from 2-methylbutane as white crystals; mp 56.6 °C; UV_{max} (log ϵ) in methylcyclohexane 264 (3.90) and 241 (4.07) nm; IR (KBr) 3385 cm^{-1} (NH); NMR ($CDCl_3$) 2.2 (6 H, singlet), 2.3 (3 H, singlet), 5.1 (1 H, singlet), 6.4–7.3 (7 H, multiplet); anal. found (calcd) C 85.1 (85.3), H 8.21 (8.05), N 6.47 (6.63). One gram (0.005 mol) of 2,4,6-trimethyldiphenylamine and 2 g (0.014 mol) of trimethyl phosphate were very slowly heated (fuming has to be avoided) to 200 °C under N_2 and stirred for 3 h. After cooling 100 mL of NaOH (13%) were added, the mixture refluxed for 2.5 h under N_2, the solution extracted with ether, and the extract dried with Na_2SO_4 and evaporated. The residue was chromatographed on Al_2O_3 with cyclohexane–CCl_4 1:1 and further purified with preparative GC (1.72 m column, i.d. 25 mm, 5% silicone rubber SE 52 on Celite 60–100 mesh, gas flow rate 1200 mL/min, column temp. 180 °C); yield, 0.2 g (20%) *N*-methyl-2,4,6-trimethyldiphenylamine; white crystals; mp 26 °C; UV_{max} (log ϵ) in methylcyclohexane 310 (3.43), 283 (3.75), 247 (4.27) nm; NMR ($CDCl_3$) 2.1 (6 H, singlet), 2.35 (3 H, singlet), 3.2 (3 H, singlet), 6.3–7.3 (7 H, multiplet).

Solvents. Methylcyclohexane (Baker) and 2-methylbutane (Baker) were distilled and chromatographed.[13] Decalin (Baker) was diluted by 2-methylpentane (1:1), chromatographed, and separated thereafter from 2-methylpentane by distillation.

Irradiation. Spectroscopic irradiations were performed with about 5 $\times 10^{-5}$ M solutions of the amines in 1 $\times$ 1 cm^2 quartz cells with MCH as solvent. The solutions were degassed on a high vacuum line, using the freeze–pump–thaw technique, and sealed off. The cooling technique of Fischer[14] was applied for irradiations at low temperatures. Preparative irradiations of A and A_d were performed in a thermostated 1 L Pyrex vessel. A medium pressure Hg lamp (Quartzlampenges. Hanau, Model TQ 150) was placed inside the vessel, separated from the solution by a filter liquid (0.1 g/L of $K_2Cr_2O_4$ and 140 g/L of $CoSO_4 \cdot 7H_2O$ in water, thickness 1 cm, transparent for 313 nm) and a vacuum mantle. TMA solutions were placed in a quartz vessel and illuminated at 254 nm with a Rayonet RPR 100 reactor. A styrofoam Dewar with four 20 cm long quartz windows made of evacuated quartz tubing with rectangular cross section (4 $\times$ 15 mm^2) surrounded the quartz vessel which was cooled with a thermocouple-controlled stream of liquid nitrogen. The extent of the reaction was controlled by measuring the UV spectra of small samples taken from the solution. During the irradiation the solutions were bubbled with nitrogen. After irradiation the solvent was partly evaporated at room temperature with a stream of nitrogen. The concentration of the solutions was 10^{-3} M and the volume was 600–800 mL.

Separation of Reaction Products. The volume of the irradiated solutions of A and of A_d was reduced to 100 mL as described above and treated with concentrated HCl. C and *N*-methyl-1,3,6,8-tetradeuteriocarbazole remained in the organic phase. After fourfold dilution of the HCl phase with water the other reaction products precipitated. The dihydrocarbazoles formed from TMA were isolated by means of preparative GC (see under *N*-methyl-2,4,6-trimethyldiphenylamine for conditions).

Spectra. UV spectra were recorded on a Cary 17 and IR spectra on a Perkin-Elmer Model 257 recording spectrophotometer. Mass spectra were measured on a Varian MAT Model CH 7 instrument at 70 eV and NMR spectra on a Varian T 60 (60 MHz) or on a Bruker WH 270 pulse fourier transform (270 MHz) instrument. For analytical gas chromatography a Perkin-Elmer Model F 7 and for preparative gas chromatography a Perkin-Elmer Model F 21 chromatograph were used.

Flash Photolysis. The flash apparatus has been described elsewhere.[2m] Solutions (1 $\times 10^{-4}$ M) of the amines in MCH were degassed and cooled as described above for spectroscopic irradiation.

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(14) Fischer, E. *Mol. Photochem.* 1970, *2*, 99–102.

Heterogeneous Photosynthetic Production of Amino Acids at Pt/TiO$_2$ Suspensions by Near Ultraviolet Light

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Abstract: Studies of the previously reported production of amino acids (glycine, alanine, serine, aspartic acid, glutamic acid) from methane, ammonia, and water in contact with irradiated suspensions of Pt/TiO_2 were extended. Products were analyzed by LC, HPLC, and coupled GC/mass spectroscopy. Analysis of product mixtures also shows the presence of MeOH, EtOH, and CH_3NH_2 as products of the photoprocess. Experiments with nitrogen-15 labeled ammonia showed that the nitrogen in the amino acids originated with the NH_3 rather than from contaminants. Amino acids were also produced from the CH_4–NH_3–H_2O mixture during decomposition of hydrogen peroxide at Pt foil. A mechanism for the reaction based on free-radical reactions initiated by hydroxyl radical produced at the irradiated catalyst is proposed.

A previous communication from this laboratory[1] described the production of amino acids by xenon lamp irradiation of platinized TiO_2 powders (Pt/TiO_2) suspended in aqueous ammoniacal solutions saturated with methane. The process apparently occurs by a photosynthetic (energetically uphill) reaction driven by the absorption of the near-ultraviolet (λ <405 nm) radiation by the TiO_2. These reaction conditions for amino acid formation from a simple reducing mixture are mild compared to previous methods for amino acid production that involved electrical discharge or very short wavelength radiation.[2]

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(1) Reiche, H.; Bard, A. J. *J. Am. Chem. Soc.* 1979, *101*, 3127.

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