One-electron photooxidation of carbazole in the presence of carbon tetrachloride. Part II. Carbon tetrachloride as a reaction medium. Use of ammonia after irradiation and during irradiation

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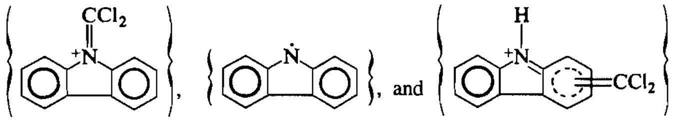
In part I of this series of papers we proposed the mechanism of electron transfer as the primary photochemical reaction in the carbazole – carbon tetrachloride system along with a secondary photochemical reaction initiated by transformations of the radical cation of carbazole in the solvent cage resulting in intermediates:



α β $\gamma_i (i = 1, 2, 3, \text{or } 4)$

In this paper we discuss the influence of ammonia, used *after* and *during* irradiation, on the mechanism of secondary transformation and the formation of thermodynamically stable products in the system studied. Such compounds as *N*-cyanocarbazole, 1-cyanocarbazole, and 3-cyanocarbazole have been formed as the main products during neutralization of the photolyte solution by ammonia gas. The mechanism of formation of these compounds has been explained by the chemical reaction of ammonia with cations α and γ_i. If ammonia is present in the solution of carbazole in CCl_4 during irradiation, such products as *N*,*N'*-dicarbazyl and *N*-cyanocarbazole are mainly formed along with 3-(*N*-carbazyl)carbazole, 3,9-di-(*N*-carbazyl)carbazole, and *N*-cyano-3-(*N*-carbazyl)carbazole. In such a case, reactions of radicals β are the determining factors in the secondary photochemical transformations. Radicals β are formed by the reaction involving ammonia with radical cations of carbazole. All the results in this paper have been discussed taking under consideration the influence of the reaction media on the mechanism of photochemical transformation of carbazole.

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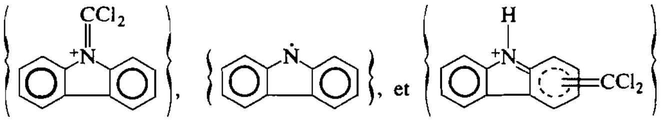
Dans la première partie de cette série d'articles nous avons suggéré que le mécanisme photochimique primaire lors de la réaction du carbazole et du tétrachlorure de carbone en était un de transfert électronique. La réaction photochimique secondaire consiste en la transformation du radical cation du carbazole dans la cage du solvant pour donner les intermédiaires suivants:



α β $\gamma_i (i = 1, 2, 3, \text{ou } 4)$

Dans cet article, nous discuterons de l'influence de l'ammoniac utilisé *après* et *avant* l'irradiation, sur le mécanisme secondaire de transformation et de formation de photoproduits thermodynamiquement stables. Lorsque l'ammoniac est ajouté après l'irradiation, le cyano-*N* carbazole, le cyano-1 carbazole et le cyano-3 carbazole ont été surtout obtenus. Ce résultat s'explique par la réaction de l'ammoniac avec les cations α et γ_i. Si au contraire, l'ammoniac est présent dans la solution du carbazole dans le CCl_4 au cours de l'irradiation, les produits suivants sont obtenus avec un bon rendement: dicarbazyl-*N*,*N'* et cyano-*N* carbazole. Les produits suivants sont également obtenus: (carbazyl-*N*)-3 carbazole, di-(carbazyl-*N*)-3,9 carbazole et cyano-*N*(carbazyl-*N*)-3 carbazole. Les radicaux β sont alors impliqués dans la transformation photochimique. Ces radicaux β sont produits suite à la réaction de l'ammoniac avec les radicaux cations du carbazole. Tous les résultats sont discutés en tenant compte de l'influence du milieu réactionnel sur le mécanisme de la transformation photochimique du carbazole.

Introduction

Among various halocarbons, carbon tetrachloride is most frequently used as a fluorescence quencher of different aromatic molecules (1–8). Studies of the mechanism of fluorescence quenching by halocarbons focused the attention of researchers upon the possibilities of photochemical reaction in the electron donor molecule – CCl_4 system. Therefore CCl_4 became used as the medi-

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TABLE 1. Photochemical reaction products of carbazole in the presence of CCl_4

No.	Compound	Reaction medium	
		$CCl_4(NH_3)$	CCl_4-NH_3
C	Carbazole	s[†]	s
1	Hexachloroethane	b	b
2	*N*-Trichloroethylenecarbazole	b	
3	1-Chlorocarbazole	b	b
22	3-Chlorocarbazole	b	b
23	N,N′-Dicarbazyl		a
24	3,9-Di-(*N*-carbazyl)carbazole		b
25	*N*-Cyanocarbazole	a	a
26	*N*-Cyano-3-(*N*-carbazyl)carbazole*		b
27	3-(*N*-Carbazyl)carbazole		b
28	1-Cyanocarbazole	a	b
29	3-Cyanocarbazole	a	b

*New compound.

[†] Abbreviations: a, main product of the reaction studied (chemical yields between 5 and 20%); b, minor product of the reaction studied (chemical yields below 5%); s, remaining substrate.

um or as the active component of the medium for photochemical reaction of many potential electron donors (8–16). Such studies not only strongly supported the electron transfer mechanism used to explain the fluorescence quenching but also depicted new possibilities of the application of an electron acceptor like CCl_4 in photochemical synthesis.

Because of its significant electron affinity (4), CCl_4 forms weak CT complexes with numerous electron donor molecules in their electronic ground state (2, 8, 13, 17–20). The excited states of aromatic molecules are therefore expected to be involved in charge transfer interactions with CCl_4 through exciplex formation. Low energy of the C—Cl bond in CCl_4 (21) and also the low activation energy of the dissociative process of electron attachment (22) promote the chemical activity of carbon tetrachloride. Therefore the electronic excitation of the electron donor molecule in the presence of CCl_4 is accompanied by the process of electron transfer to the CCl_4 molecule according to the scheme

$$e^- \text{ (donor)} + CCl_4 \rightarrow \dot{C}C_3 + Cl^-$$

which is the primary photochemical process initiating complex reactions.

Among aromatic amines known as typical electron donors, carbazole turned out to be an interesting subject of studies of the photophysical and photochemical properties in the presence of halocarbon molecules. The carbazole–CCl_4 system in the electronic donor ground state did not show any significant interaction of electron donor–acceptor type. Nevertheless, such interactions appear in the first electronic excited singlet state of the carbazole molecule. This has been supported by studies on the photophysical properties of the carbazole–CCl_4 system in various media (1), as well as by the fact that fluorescence quenching of carbazole by CCl_4 is accompanied by a photochemical reaction (14). The proposed mechanism of the photochemical transformations in the carbazole–CCl_4 system has been discussed in detail in part I of this series of papers (15). This paper is a continuation of the discussion of the photochemical reactions involved in the carbazole–CCl_4 system, considering this time the influence of ammonia on the formation of the thermodynamically stable products after irradiation as well as the influence of ammonia on the mechanism and products during irradiation.

Results and discussion

Irradiation of solutions of carbazole in carbon tetrachloride gives rise to the formation of both stable products such as hexachloroethane (**1**), *N*-trichloroethylenecarbazole (**2**), 1-chlorocarbazole (**3**), and 3-chlorocarbazole (**22**), as well as reactive transient photoproducts stable only in the CCl_4 medium. When, after irradiation of carbazole in CCl_4, the photolysis solution was saturated with ammonia gas to neutralize the formation of hydrogen chloride, the reactive products underwent transformation to the corresponding cyano derivatives of carbazole. It turned out that *N*-cyanocarbazole (**25**), 1-cyanocarbazole (**28**), and 3-cyanocarbazole (**29**) are the main products formed from these transformations (first column in Table 1). We have also performed the irradiation of carbazole solution in CCl_4 saturated with ammonia gas. In this case *N*,*N*′-dicarbazyl (**23**) and **25** are the main products of the reaction. We have also identified the following compounds: 3,9-di-(*N*-carbazyl)carbazole (**24**), *N*-cyano-3-(*N*-carbazyl)carbazole (**26**), and 3-(*N*-carbazyl)carbazole (**27**) in addition to products **1**, **3**, **22**, **28**, and **29** (second column in Table 1).

All the isolated and identified products, using ammonia after and during irradiation, support the carbazole radical cation transformation mechanism that we proposed in part I (15).

These results, along with the known electron acceptor properties of CCl_4 as well as the photophysical properties of aromatic electron donor – CCl_4 systems (1–4), strongly support the mechanism of the primary photochemical reaction in the carbazole–CCl_4 system according to the following:

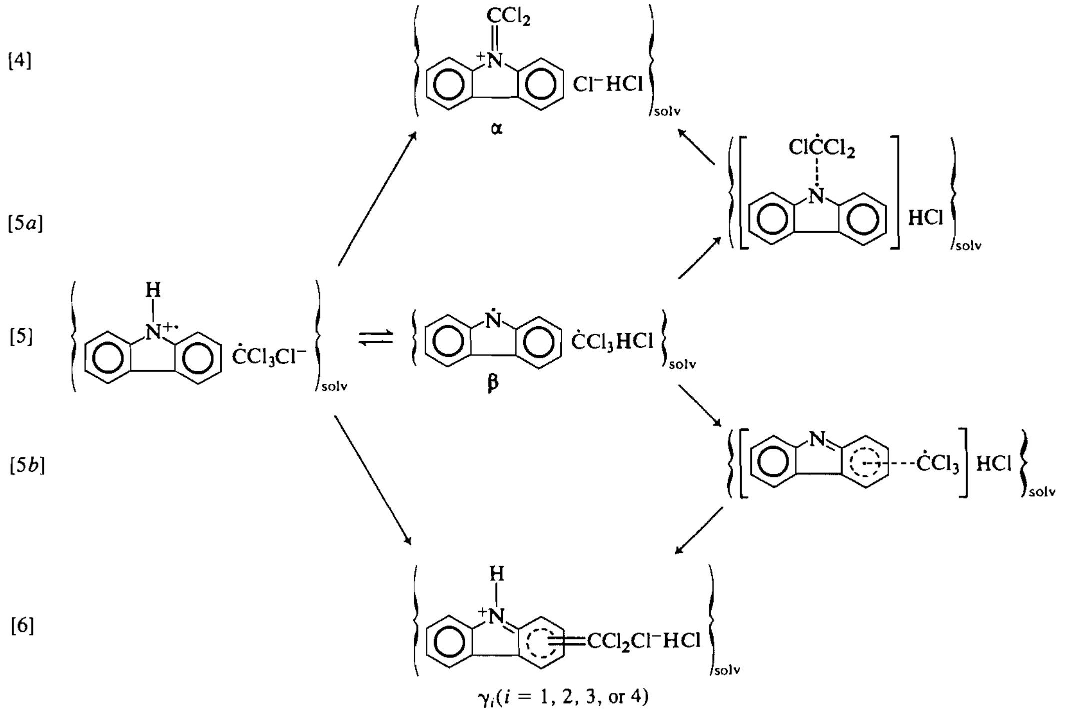
$$[1] \quad C + \hbar\nu \rightarrow {}^1C^*$$

$$[2] \quad {}^1C^* + CCl_4 \rightarrow {}^1(C^{\delta+} \cdots CCl_4{}^{\delta-})^*_{solv}$$

$$[3] \quad {}^1(C^{\delta+} \cdots CCl_4{}^{\delta-})^*_{solv} \rightarrow [C^{+\cdot}\ Cl^-\ \dot{C}Cl_3]_{solv}$$

The electron transfer from the electronically excited carbazole molecule to the CCl_4 molecule in the excited CT complex (eq. [3]) gives rise to chemical transformation in the system studied. The radical cation of carbazole, chloride ion, and trichloromethyl radical are the primary products of the photochemical reaction.

The secondary reactions in the solvent cage are illustrated by the following scheme:

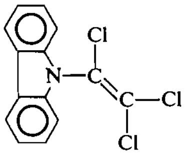


SCHEME 1

The possibilities of transformations of the carbazole radical cation are conditioned by the presence of trichloromethyl radical and chloride ion in the solvent cage. The reaction of the radical cation of carbazole with the trichloromethyl radical can occur with the participation of the nitrogen as well as the ring leading to the formation of the transient ionic products α and γ_i (mainly with $i = 1$ or 3). The transformations of the radical cation of carbazole in the solvent cage are accompanied by the formation of thermodynamically stable molecules of hydrogen chloride (eqs. [4] and [6]). On the other hand, the radical cation of carbazole in the presence of chloride ion in the solvent cage can also split off a proton, transforming itself into the radical β. Reaction [5] is reversible (23, 24) because the N—H and H—Cl bond energies are about the same (~431 kJ mol^{-1}) (25). So, in the presence of HCl in the solvent cage, radical β can undergo inverse transformation to the carbazole radical cation or can react with the trichloromethyl radical. The reaction of radical β with radical CCl_3 can lead to cation α (eq. [5*a*]) as well as to cation γ_i (eq. [5*b*]). In each of these reactions chloride ion is being split off.

C_2Cl_6

1



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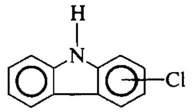
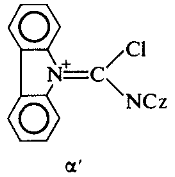
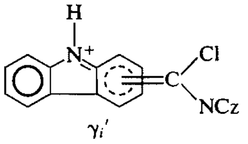


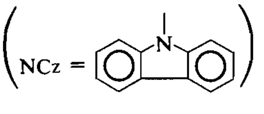
3, 22



α′



γ_i'



Apart from the reactions in the solvent cage discussed above, both the radical cation of carbazole and the trichloromethyl radical, as well as intermediate products α, β, and γ_i, participate in the secondary reactions outside the solvent cage. This has been depicted by the nature of the photochemical compounds obtained, such as **1**, **2**, **3**, and **22**, as well as compounds α′ and γ_i' which are of intermediate character. The formation mechanism of these products has been proposed and discussed previously (15) and we do not intend to go into further details here.

Acidic reaction media do not favour the formation of *N*,*N*′-dicarbazyl. The lack of this product can be interpreted by the low concentration of radicals β caused by the shift of the equilibrium of reaction [5] towards the radical cation of carbazole and by reactions [5*a*] and [5*b*].

Photochemically generated trichloromethyl radicals initiate chain reactions in the solution according to the scheme:

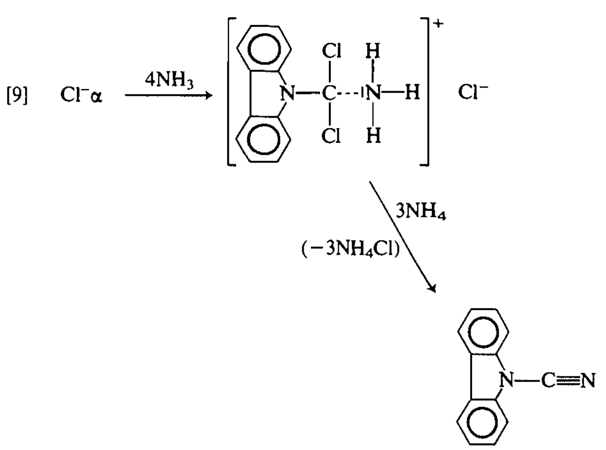
$$[7] \qquad C + \dot{C}Cl_3 \xrightarrow[(-HCl)]{CCl_4} \gamma_i\, Cl^- + \dot{C}Cl_3$$

$$[8] \qquad (\alpha \text{ or } \gamma_i) + \dot{C}Cl_3 \xrightarrow[(-HCl)]{CCl_4} (\text{disubstituted monocations}) + \dot{C}Cl_3$$

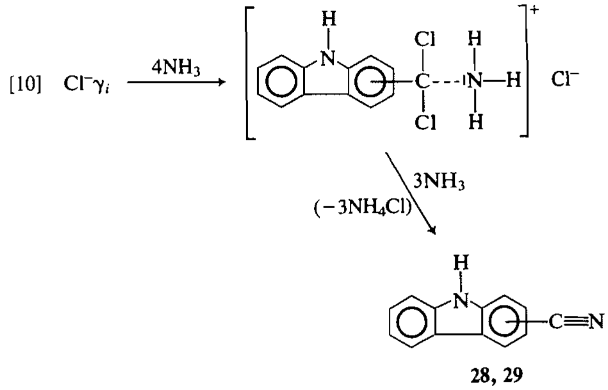
Significant photochemical activity of carbazole solution in CCl_4 can be explained by reactions [3] and [7]. Reaction [8] acts as a source of disubstituted monocations in the solution studied.

Use of NH_3 after irradiation

After saturation of the photolysis solution by ammonia gas, products such as **25**, **28**, and **29** appeared in addition to ammonium chloride among the other compounds of the reaction. This points to the fact that reactive transient products, stable in the CCl_4 medium, easily undergo reaction in the presence of ammonia to the corresponding cyano derivatives of carbazole. Therefore the formation of products **25**, **28**, and **29** can be presented by the following ammonolysis mechanism of intermediates α and γ_i:



25

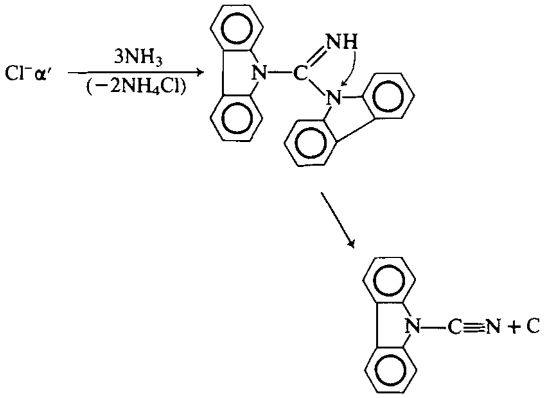


28, 29

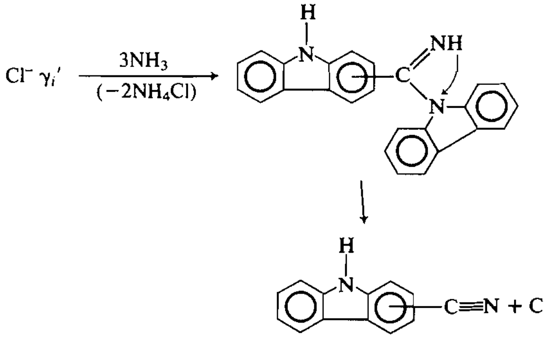
Reactions [9] and [10] are the main sources of these products. In a similar way, intermediates α′ and γ_i' might undergo reaction in the presence of ammonia resulting in the corresponding (carboimino-*N*-carbazyl)carbazoles. These, in turn, can undergo rearrangement to cyano derivatives of carbazole.

We propose the following scheme for these reactions:

[11]



[12]



The presence of ammonia in excess, acting as a good scavenger of HCl in the reaction medium, favours the course of reactions [9] to [12].

Decomposition of (carboimino-*N*-carbazyl)carbazoles to carbazole and cyano derivatives of carbazole in reactions [11] and [12] requires a certain activation energy. Therefore, at room temperature, it can take place only partially in the photolyte solution. This reaction occurs mainly on the surface of silica gel during chromatographic separation of products.

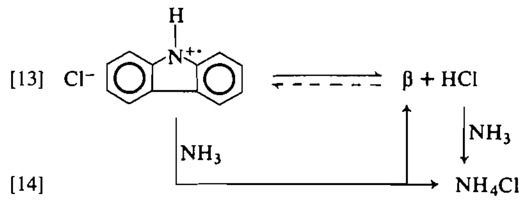
When nonactivated silica gel, containing the adsorbed water on its surface, was used, we found (carbo-*N*-carbazyl)carbazoles in the separation fractions. This confirms the presence of (carboimino-*N*-carbazyl)carbazoles in the mixture of products chromatographically analysed. The formation of (carbo-*N*-carbazyl)carbazoles in this case can only be explained by hydrolysis of (carboimino-*N*-carbazyl)carbazoles. Similar reactions have been discussed in the literature (26). We failed to isolate (carboimino-*N*-carbazyl)carbazoles because of the chemical properties mentioned above. The formation mechanism and the chemical properties of these compounds require extended studies.

If the irradiated solution of carbazole in CCl_4 is saturated with ammonia gas the main reaction products are as follows: *N*-cyanocarbazole, 1-cyanocarbazole, and 3-cyanocarbazole. It is an indication of the fact that positions 1, 3, 6, 8 and 9(N) are likely to be favoured in the transformations of both the radical cation of carbazole and the carbazyl radical β in the solvent cage. The same principle of transformation for the radical cation of carbazole has been observed in the studies of electrochemical oxidation of carbazole (27). Similarly, the photolysis products of *N*-acetyl carbazole, being formed as a result of the reactions of carbazyl and acetyl radicals in the solvent cage (28), as well as the thermal rearrangement products of *N*,*N*′-dicarbazyl (29), strongly support the mechanism discussed for the reactions between the pair of radicals β and CCl_3. These experimentally observed chemical properties of the radical cation of carbazole as well as of radical β are in good agreement with theoretical estimations of the electron charge density in the carbazole molecule (27, 30) and in the carbazyl radical (28).

As we have shown before (15), the radical cation of carbazole can also undergo chemical transformations through positions 2 and 4 but with much less probability than through positions 1 and 3. It is presumably the reason for the low yields of 2-cyanocarbazole and 4-cyanocarbazole in the reaction medium studied. We failed to isolate these products in an amount sufficient for unambiguous identification. Similarly, because of the low yields, we did not manage to isolate dicyano derivatives of carbazole which can be formed as the result of ammonolysis of disubstituted monocations.

Use of NH_3 during irradiation

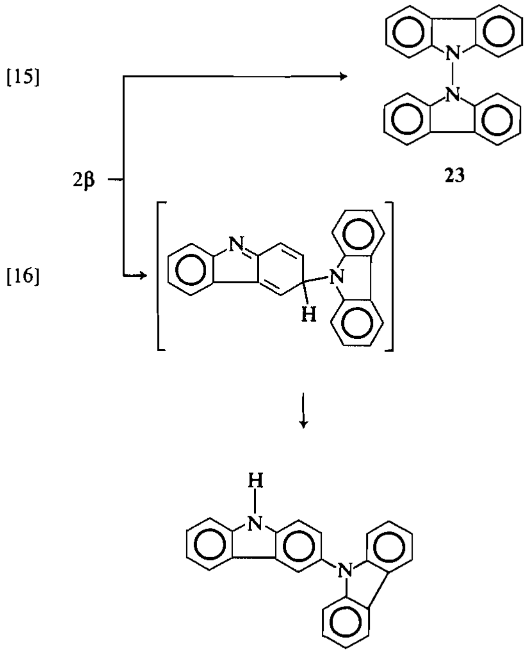
The course of photochemical transformations in the carbazole–CCl_4 system, discussed above, is radically changed in the presence of ammonia. This is indicated by the qualitative and quantitative composition changes of the photochemical reaction products. The products obtained (see Table 1) show the participation of the radicals β in the secondary reactions. Thus, it may be suggested that the reaction medium favours the formation of the radicals β. Therefore, the active role of ammonia in the reaction medium could be explained by the removal of hydrogen chloride from the reaction medium and also by interaction with the radical cation of carbazole out of the cage according to the following scheme:



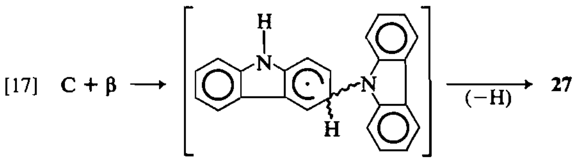
SCHEME 2

Scheme 2 explains the mechanism of formation of the radicals β in the reaction medium. Active interaction between ammonia and radical cations of aromatic amines is well known in the literature (10, 11, 31, 32). The results in these papers show that such interaction usually leads to the transformation of radical cations of aromatic amines to the corresponding radicals.

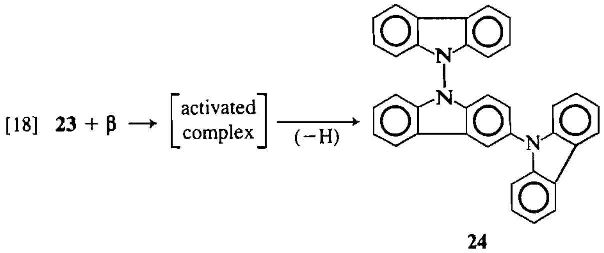
The reactions involving the recombination of radicals β explain explicitly the formation mechanism of such products as **23** and **27**:

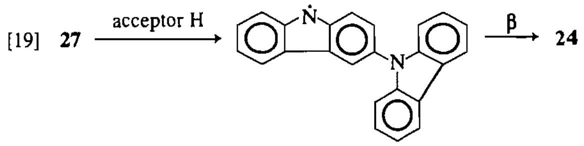


The interaction between radicals β and the carbazole molecule in the presence of hydrogen acceptor may also lead to the formation of product **27** according to reaction [17].

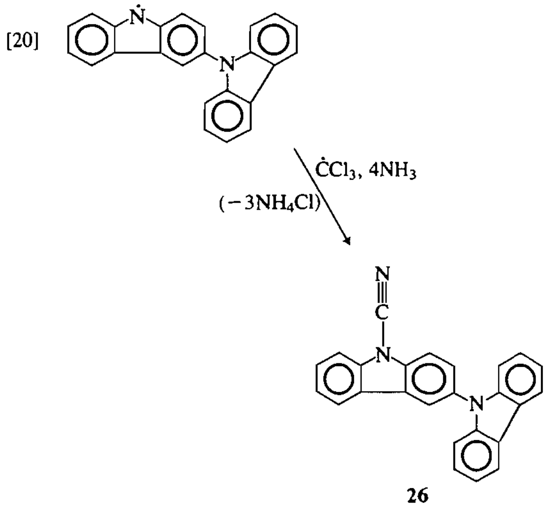


Because the medium favors radical reactions, products **23** and **27** partially undergo further transformation. This is indicated by the formation of product **24** according to reactions [18] and [19].





Radicals 3-(*N*-carbazyl)carbazyl appearing in reaction [19] can undergo not only the recombination reaction with radicals β forming trimer **24** but they can recombine with each other resulting in the tetramer 3,3′-di(*N*-carbazyl)-*N*,*N*′-dicarbazyl (33). In the reaction medium studied, radicals 3-(*N*-carbazyl)carbazyl, in the presence of trichloromethyl radicals, can also be the precursor of product **26** according to reaction [20].



Another possible formation mechanism of **26** can be described by reaction of radical β with *N*-cyanocarbazole:

$$[21]\quad \mathbf{25} + \beta \longrightarrow \begin{bmatrix}\text{activated}\\ \text{complex}\end{bmatrix} \xrightarrow[(-\text{H})]{} \mathbf{26}$$

Intermediate radical products as well as CCl_4 can be hydrogen acceptors in reactions [15]–[19] and [21].

Reactions [15]–[21] indicate the role played by radical β in the formation mechanism of products **23**, **27**, **24**, and **26**. Reactions involving radicals β have been thoroughly studied previously (33). Products **23**, **27**, and **24** are also formed during the chemical oxidation of carbazole with nickel peroxide (34). Thus, some analogies can be observed between photochemical and chemical oxidation of carbazole.

The products presented above along with results described in refs. 33 and 34 indicate that the production of radicals β is always accompanied by the formation of polycarbazoles according to the simplified scheme:

$$\beta \xrightarrow{\beta} (\text{dimers}) \xrightarrow[(-H)]{\beta} (\text{trimers}) \xrightarrow[(-H)]{\beta} \cdots$$

Furthermore these products prove also that radicals β outside the solvent cage take part in the reactions mainly at positions 3 and 9.

Intermediates α and γ_i are also formed in the reaction medium studied; they are indicated by the formation of products **25**, **28**, and **29** described by reactions [9] and [10]. Products **28** and **29** are formed with low yields, while **25** as well as **23** are the main products of the discussed photochemical transformation of carbazole.

These studies of the photochemical reaction products lead to the assumption that the probability of transformation of the carbazole radical cation to form the intermediates α and γ_i (eqs. [4] and [6] in the presence of ammonia decreases in favour of the formation of radical β (eq. [5]).

The significant yields of products **23** and **25** are connected with the high concentration of β radicals in the reaction medium. Product **23** is formed in reaction [15], while the formation of **25** can be explained by reaction [5*a*] which occurs mainly outside the solvent cage.

All the results discussed in parts I and II will serve as an excellent background for our future spectroscopic and quantitative studies of photochemical reactions in the carbazole–CCl_4 system.

Experimental

Apparatus

The ^1H nmr spectra have been measured with a Bruker WH-90 spectrometer operating at 90 MHz. Chemical shift values are given in a δ scale with respect to TMS as an internal standard. Infrared spectra were recorded on a Perkin–Elmer 710B infrared spectrophotometer and mass spectra were taken with a AEI MS902 mass spectrometer.

Materials

Carbazole was an Eastman Organic Chemical and was used without any further purification. Carbon tetrachloride from American Chemicals was a Spectrograde quality and it was purified as described previously (15). Petroleum ether (boiling range 30–75°C) and benzene were distilled before use.

General procedure

Carbazole solution (0.005 *M*) in carbon tetrachloride was deoxygenated with oxygen-free argon and irradiated in a Pyrex Hanovia immersion-well reactor for 1 hour with an Hanovia 679A36 450 W medium-pressure mercury lamp. After irradiation, the solution of photolyte was saturated with ammonia gas, so that hydrogen chloride generated during the reaction was neutralized. Following that, the solution of photolyte was concentrated.

Irradiation of carbazole solution (0.005 *M*, 1 h) in carbon tetrachloride was also carried out in the presence of NH_3. A slow stream of ammonia gas was bubbled through the solution before and during irradiation. Hydrogen chloride generated during the photochemical reaction was thus removed from the reaction medium. When irradiation was finished, the solution of photolyte was concentrated.

The photochemical products were then analysed by tlc detected by uv (using Eastman–Kodak tlc plates, silica gel 13181) and separated by column chromatography. The columns were packed with silica gel (Kieselgel 60, Merck, particle size 0.040–0.063 mm). Developing systems consisted of petroleum ether (low boiling fraction) and ethyl ether or benzene. The developed distance on tlc plates was kept at 10 cm. Identified products, on the basis of their ^1H nmr, ir, and mass spectra, have been listed in Table 1 and their R_f values on tlc plates with silica gel are listed in Table 2.

Spectral characteristics of the photochemical products

Hexachloroethane (**1**): single crystals. The compound was identified as described previously (15).

N-*Trichloroethylenecarbazole* (**2**): crystalline solid and *1-chlorocarbazole* (**3**): crystalline solid. These compounds were identified as described previously (14, 15).

3-Chlorocarbazole (**22**): crystalline solid; ir (film) $\bar{\nu}_{max}$: 3390 (vs, N—H), 1610 (w), 1590 (w), 1560 (w), 1460 (m), 1440 (s), 1430 (s), 1320 (m), 1280 (w), 1260 (m), 1230 (w), 1210 (vw), 1190 (w), 1095 (w), 1055 (m), 1040 (w), 1010 (vw), 990 (w), 915 (m), 865 (s), 800 (vs), 735 (s), 710 (s) cm^{-1}; ^1H nmr (acetone-d_6) δ: 7.09–7.58 (m, 5H, arom), 8.11–8.22 (m, 2H, arom), 10.52 (s, br, 1H, N—H); ($CDCl_3$): 7.10–7.50 (m, 5H, arom), 7.90–8.15 (m, 2H, arom and 1H, N—H); mass spectrum (70 eV) (mol. wt. for $C_{12}H_8NCl$: 201.66), *m/e*: 203 (M^+, 30), 201 (M^+, 100), 167 (6), 166 (37), 165 (6), 164 (9), 140 (10), 139 (13).

N,N′-*Dicarbazyl* (**23**); crystalline solid. The compound was identified as described previously (14).

*3,9-Di-(*N-*carbazyl)carbazole* (**24**): crystalline solid; ir (film) $\bar{\nu}_{max}$: 1615 (m), 1595 (m), 1575 (w), 1490 (s), 1475 (s), 1450 (vs), 1320 (m), 1305 (s), 1265 (m), 1225 (vs), 1160 (w), 1145 (w), 1105 (w), 1015 (m), 1000 (w), 990 (w), 960 (vw), 920 (w), 910 (w), 870 (vw), 840 (vw), 800 (m), 740 (vs), 715 (s) cm^{-1}; ^1H nmr ($CDCl_3$) δ: 6.93–7.18 and 7.18–7.55 (2 complex m, 17H, arom), 8.10–8.29 (m, 5H, arom), 8.36 (d, J = 1.5 Hz, 1H, arom); mass spectrum (70 eV) (mol. wt. for $C_{36}H_{23}N_3$: 497.60), *m/e*: 497 (M^+, 12), 332 (43), 331 (100), 330 (22), 329 (20), 167 (75), 166 (58), 165 (25), 140 (42), 139 (27).

N-*Cyanocarbazole* (**25**): crystalline solid. The compound was identified as described previously (14).

N-*Cyano-3-(*N-*carbazyl)carbazole* (**26**): crystalline solid; ir (film) $\bar{\nu}_{max}$: 2220 (vs, C≡N), 1610 (w), 1580 (m), 1565 (w), 1485 (vs), 1470 (s), 1445 (vs), 1350 (w), 1320 (s), 1300 (s), 1260 (w),

TABLE 2. R_f values of the photoproducts in the carbazole–CCl_4 system

	Developing system (v/v)			
	Petroleum ether – ethyl ether			
No.*	100:1	10:1	2:1	Benzene
C	0.05	0.22	0.57	0.76
2	0.74	0.82	0.86	0.91
3	0.23	0.53	0.77	0.84
22	0.04	0.14	0.40	0.73
23	0.54	0.77	0.84	0.91
24	0.32	0.68	0.82	0.90
25	0.22	0.57	0.78	0.77
26	0.09	0.41	0.75	0.79
27		0.06	0.28	0.72
28		0.08	0.44	0.27
29		0.02	0.14	0.24

*Notation of compounds is the same as in Table 1.

1220 (s), 1150 (w), 1135 (w), 1100 (w), 900 (w), 860 (vw), 830 (vw), 795 (m), 735 (vs), 710 (s), cm^{-1}; ^1H nmr ($CDCl_3$) δ: 7.17–8.22 (complex m, 15H, arom); mass spectrum (70 eV) (mol. wt. for $C_{25}H_{15}N_3$: 357.42), *m*/*e*: 357 (M^+, 100), 330 (11), 165 (30), 138 (8).

*3-(*N*-Carbazyl)carbazole* (**27**): crystalline solid; ir (film) $\tilde{\nu}_{max}$: 3385 (vs, N—H), 1610 (w), 1580 (m), 1560 (w), 1490 (vs), 1470 (s), 1455 (vs), 1445 (vs), 1360 (vw), 1320 (s), 1305 (s), 1260 (m), 1225 (vs), 1145 (m), 1130 (m), 1095 (vw), 1000 (w), 990 (w), 900 (m), 860 (vw), 825 (w), 795 (m), 740 (vs), 710 (s), cm^{-1}; ^1H nmr ($CDCl_3$) δ: 7.16–7.67 (m, 11H, arom), 7.95–8.30 (m, 4H, arom and 1H, N—H); (acetone-d_6): 7.18–7.87 (m, 11H, arom), 8.13–8.40 (m, 4H, arom), ~10.72 (broad band, 1H, N—H); mass spectrum (70 eV) (mol. wt. for $C_{24}H_{16}N_2$: 332.41), *m*/*e*: 332 (M^+, 100), 166 (34), 165 (27), 139 (12).

1-Cyanocarbazole (**28**): crystalline solid; ir (Nujol film) $\tilde{\nu}_{max}$: 3300 (s, N—H), 2200 (s, C≡N), 1615 (vw), 1595 (m), 1570 (vw), 1490 (w), 1425 (m), 1325 (w), 1315 (m), 1265 (w), 1235 (m), 1220 (w), 1205 (w), 1105 (w), 780 (w), 725 (s), 710 (s) cm^{-1}; ^1H nmr (acetone-d_6) δ: 7.19–7.83 (complex m, 5H, arom), 8.16, 8.24 and 8.40, 8.48 (2d, 2H, arom), 11.13 (s, br, 1H, N—H); ($CDCl_3$): 7.18–7.74 (complex m, 5H, arom), 8.04, 8.12 and 8.22, 8.30 (2d, 2H, arom), 8.97 (s, 1H, N—H); mass spectrum (70 eV) (mol. wt. for $C_{13}H_8N_2$: 192.22), *m*/*e*: 192 (M^+, 100), 191 (7.1), 165 (7.8), 164 (14.2), 138 (4.2), 96 (8.5).

3-Cyanocarbazole (**29**): crystalline solid; ir (Nujol film) $\tilde{\nu}_{max}$: 3275 (s, N—H), 2200 (s, C≡N), 1615 (w), 1590 (s), 1570 (vw), 1480 (w), 1395 (w), 1325 (w), 1315 (m), 1275 (w), 1230 (s), 1205 (w), 1190 (m), 1110 (w), 885 (m), 800 (s), 755 (w), 735 (m), 720 (s) cm^{-1}; ^1H nmr (acetone-d_6) δ: 7.19–7.69 (m, 5H, arom), 8.20, 8.29 (d, 1H, arom), 8.58 (s, 1H, arom), 10.92 (s, br, 1H, N—H); ($CDCl_3$): 7.24–7.73 (m, 5H, arom), 8.04, 8.13 (d, 1H, arom), 8.38 (s, 1H, arom), ~8.48 (s, 1H, N—H); mass spectrum (70 eV) (mol. wt. for $C_{13}H_8N_2$: 192.22), *m*/*e*: 192 (M^+, 100), 191 (11.3), 165 (13.4), 164 (17.4), 138 (7.1), 96 (15.6).

Conclusions

Use of ammonia *after* irradiation of the carbazole solution in CCl_4 leads to the appearance of *N*-, 1-, and 3-cyanocarbazoles as the main products in the reaction mixture. The formation of these products indicates that chemical reaction take place between ammonia and intermediates α and γ_i. This strongly supports the proposed mechanism of transformations of the radical cation of carbazole.

When ammonia was used *during* irradiation of the carbazole solution in CCl_4 we obtained *N*,*N*′-dicarbazyl and *N*-cyanocarbazole as the main products in addition to 3-(*N*-carbazyl)carbazole, 3,9-di-(*N*-carbazyl)carbazole, and *N*-cyano-3-(*N*-carbazyl) carbazole. The formation of these products is closely connected with the reactions of radicals β. Radicals β along with intermediates α and γ_i also serve as a proof for the presence of radical cations of carbazole in the photochemical reaction medium.

All the intermediate products of the photochemical reaction in the carbazole–CCl_4 system indicate that the primary photochemical process is the electron transfer from the singlet excited molecule of carbazole to the CCl_4 molecule in the excited CT complex, $^1(C^{\delta+}\cdots CCl_4^{\delta-})^*$. Furthermore, transformation of the primary photochemical reaction products depends not only on their particular type, but also on the nature of the reaction media used.

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