One-electron photooxidation of carbazole in the presence of carbon tetrachloride. Part I. Carbon tetrachloride and ethanol used as reaction media

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This paper is dedicated to Professor Camille Sandorfy on the occasion of his 60th birthday

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The photochemical reaction products of carbazole with carbon tetrachloride in ethanol have been isolated and identified along with photoproducts in the irradiated solution of carbazole in pure CCl_4 using water and ethanol added after the irradiation. This allowed us to discuss the complex mechanism of secondary photochemical changes in the carbazole– CCl_4 system. We propose that the electron transfer from carbazole to CCl_4 molecule in the excited CT complex, ${}^{1}(C^{\delta+}\cdots CCl_4^{\delta-})^*$, is the primary photochemical reaction followed by an heterolytic dissociation of a C—Cl bond which gives rise to the primary photoproducts in the solvent cage [C⁺ Cl⁻ CCl_3]. Secondary photochemical reactions initiate transformation of the radical cation of carbazole in the solvent cage giving rise to the following intermediate species:



The probability of formation and further transformations of these transient products: α , β , and γ_i , depends strongly on the nature of the reaction media. Thermodynamically stable products are formed depending on the reaction media; (carboethoxy)carbazoles, (carbo-*N*-carbazyl)carbazoles, and carbazole – carboxylic acids can serve as a proof for the formation of the above listed intermediates. All the results reported on the secondary photochemical reactions strongly support the electron-transfer primary mechanism used to explain the fluorescence quenching of carbazole by CCl₄.

These results also explain the changes observed in the fluorescence spectrum of carbazole when the ethanol solution of carbazole in the presence of CCl_4 is irradiated.

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Nous avons isolé et identifié les produits de la réaction photochimique entre le carbazole et le tétrachlorure de carbone d'abord dans l'éthanol comme solvant mais aussi dans le CCl_4 pur utilisé comme solvant pendant l'irradiation alors que l'eau et l'éthanol étaient ajoutées au CCl_4 après l'irradiation. Ceci nous a permis de discuter du mécanisme complexe des réactions photochimiques secondaires dans le système carbazole– CCl_4 . Nous proposons que l'étape photochimique primaire soit le transfert électronique du carbazole au CCl_4 par l'intermédiaire d'un complexe de transfert de charge excité ${}^1(C^{\delta+}\cdots CCl_4^{\delta-})^*$ suivi par une dissociation hétérolytique d'un lien C—Cl donnant lien à l'apparition des photoproduits primaires [C+*Cl⁻CCl_3] dans la cage du solvant. Par réactions photochimiques secondaires, les espèces intermédiaires suivantes seraient formées dans la cage du solvant:



La probabilité de formation et également de transformation de ces espèces transitoires α , β et γ_i dépend beaucoup de la nature des milieux réactionnels. La nature des photoproduits thermodynamiquement stables formés est en fonction de la nature du milieu réactionnel. Les molécules de (carboéthoxy)carbazoles, de (carbo-*N*-carbazyl)carbazoles et d'acides carbazole – carboxylique formées démontrent bien l'importance des espèces transitoires ci-haut mentionnées dans l'élaboration du mécanisme réactionnel. Tous les résultats obtenus sur les réactions photochimiques secondaires sont en accord avec un mécanisme primaire impliquant un phototransfert électronique lequel mécanisme est responsable pour la désactivation de la fluorescence du carbazole en présence de CCl₄. Ces résultats expliquent également les modifications observées dans le spectre de fluorescence du carbazole dans l'éthanol en présence de CCl₄ au cours de l'irradiation.

Introduction

Carbon tetrachloride is a well-known fluorescence quencher of various aromatic electron donors (1-6). The mechanism of quenching is most

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commonly connected with the photochemical reaction in which CCl_4 participates as an electron acceptor, favorable conditions being created by the distinctive electron affinity of CCl_4 (2.12 eV) (7) and comparatively low C—Cl bond energy (231.2 kJ mol⁻¹) (8).

The electron transfer mechanism has proved to

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explain the fluorescence quenching of carbazole in non-polar solvents (1) whereas in hydrogen bonding solvents like ethanol, the fluorescence quenching decay rate did not follow the usual correlation with the ionization potential of the first excited singlet donor state (2). Carbazole cation-radicals have been observed when alcoholic solutions of carbazole were irradiated into the ${}^{1}L_{b}$ or the ${}^{1}L_{a}$ states of the carbazole molecule and the number of these radicals was found to increase in the presence of CCl_4 (9). The explanation of the fluorescence quenching mechanism of carbazole by CCl₄ in alcoholic solvents requires more extended studies. Therefore it became interesting to study the photochemical reaction in the carbazole-CCl₄ system in ethanol as the reaction medium. In this paper we made an attempt to discuss the photochemical reaction mechanisms responsible for all the photochemical substituted carbazoles obtained and identified when a CCl₄ solution of carbazole is irradiated in presence of ethanol or when ethanol or water were added to the photolite after irradiating the carbazole molecules in pure CCl₄.

Results and discussion

When an ethanol solution of carbazole $(1 \times 10^{-4} M)$ in the presence of CCl₄ (0.1 M) is irradiated in its longwave absorption band, the typical carbazole fluorescence disappears and new fluorescence emissions appear at approximately 375, 400, and 425 nm as can be seen in Fig. 1. The excitation spectra of these new emissions are shifted to the red compared to the excitation spectrum of carbazole. This, coupled to the fact that the charge transfer exciplex "carbazole–CCl₄" was found to be non-emissive (2), strongly suggests that these new fluorescence emissions might be due to photochemical products.

As our studies progressed we discovered that photoproducts created in the carbazole– CCl_4 system are of the transient character and are stable only in pure CCl_4 medium, but when ethanol or water are present they easily undergo further transformation giving as a result, proper mono- and di-substituted derivatives of carbazole: (carboethoxy)carbazoles, (carbo-*N*-carbazyl)carbazoles, and carbazole – carboxylic acids.

Table 1 shows the photoproducts identified from the photoreaction of carbazole with CCl_4 in ethanol as a solvent (first column) and also in pure CCl_4 (second and third columns). These photoproducts were obtained and identified when the solution was first irradiated in pure CCl_4 followed by additions of ethanol or water.



FIG. 1. Fluorescence spectra of an ethanol solution of carbazole $(1 \times 10^{-4} M)$ in the presence of CCl₄ (0.1 M) before irradiation (—), and after the specified time of irradiation in seconds (---). The excitation wavelength was fixed at 320 nm.

We found that derivatives of carbazole, namely mono-substituted in positions 1 and 3, and disubstituted in positions 1 and 6 or 3 and 9(N), are the main products obtained from the photochemical reaction of carbazole with CCl_4 .

Considering the well-known photophysical results (1, 2, 5–7, 10) and also the photochemical reaction products obtained, we propose the following primary photophysical and photochemical processes:

1]	C + hv	→	¹ C*
2]	¹ C*	\rightarrow	$C + hv_F$
[3]	$^{1}C* + CCl_{4}$	~* ~*	$^{3}C^{*} + CCl_{4}$ C + CCl ₄
[4]	$^{1}C^{*} + CCl_{4}$	~~	$^{l}(C^{\delta^{+}}\cdots CCl_{4}^{\delta^{-}})^{*}_{solv}$
		~~	${}^{3}C* + CCl_{4}$
[5]	${}^{1}(C^{\delta+}\cdots CCl_{4}^{\delta-})^{*}_{solv}$	~~	$^{1}C^{*} + CCl_{4}$ C + CCl ₄
[6]	$^{1}(C^{\delta^{+}}\cdots CCl_{4}^{\delta^{-}})_{solv}$	~	${C^+ \cdot Cl^- CCl_3}_{solv}$

The energy loss into the singlet state manifold may proceed through emission of radiation (reaction [2]) or radiationless processes via the external spin-orbital coupling with CCl_4 molecule, internal conversion (reaction [3]) or via complexation (reactions [4] and [5]). Furthermore, when transient excited CT complex is formed, electron transfer may occur from carbazole molecule to CCl_4 molecule. It is followed by an heterolytic dissociation of

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		Reaction medium [†]				
No.	Compound	CCl₄ in C₂H₅OH	CCl ₄ (C ₂ H ₅ OH)	CCl ₄ (H ₂ O)		
C	Carbazole	s	s	s		
1	Hexachloroethane	b	b	b		
2	N-(Trichloroethylene)carbazole*	b	b	b		
3	1-Chlorocarbazole		b	b		
4	N-(Carboethoxy)carbazole	b	b			
5	1-(Carboethoxy)carbazole	а	а			
6	2-(Carboethoxy)carbazole	b	b			
7	3-(Carboethoxy)carbazole	а	а			
8	4-(Carboethoxy)carbazole	а	b			
9	3,9-Di(carboethoxy)carbazole*	b	b			
10	1,3-Di(carboethoxy)carbazole*	b	b			
11	1,6-Di(carboethoxy)carbazole*	b	ь			
12	1,8-Di(carboethoxy)carbazole*	b				
13	3,6-Di(carboethoxy)carbazole	b	ь			
14	3,5-Di(carboethoxy)carbazole*	b				
15	Carbazole-1-carboxylic acid	b	ь	а		
16	Carbazole-3-carboxylic acid	b	b	а		
17	N, N'-Carbodicarbazyl*		b	а		
18	1-(Carbo-N-carbazyl)carbazole*		b	а		
19	3-(Carbo-N-carbazyl)carbazole*		b	a		
20	3,9-Di(carbo-N-carbazyl)carbazole*		b	а		
21	1,6-Di(carbo-N-carbazyl)carbazole*		b	а		

TABLE 1. Photochemical reaction products of carbazole in the presence of CC	TABLE	1. Photochemical	reaction	products	of carbazole	in the	presence	of CC
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*New compound. †a: main product of the reaction studied (chemical yields between 5 and 20%); b: other product of the reaction studied (chemical yields below 5%); s: remaining substrate.

a C—Cl bond giving rise to the possible primary products in the solvent cage (reaction [6]).

The secondary products obtained and identified along with the data published (11-20) allow us to

propose the following mechanism of transformation of the carbazole radical cation in the solvent cage:



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The electron densities calculated for the carbazole molecule show that among a variety of mesomeric structures of the radical-cation, the 1, 3, 6, 8, and 9(N) positions are likely to be favored (11, 12). This was later confirmed by the analysis of the electrochemical oxidation products of carbazole and its substituted derivatives (12, 13). Radical recombination reactions [7] and [9] in the solvent cage then become very probable, giving the intermediate ionic products α and γ_i (mainly with i = 1or 3). The presence of chlorine ion in the solvent cage makes possible the transformation of the radical-cation of carbazole to carbazvl radical B. A similar reaction has already been discussed in the literature (21). But since the N-H and H--Cl bond energies are nearly the same at 431 kJ mol⁻¹ (14), reaction [8] is probably reversible (15). However, radicals β and CCl₃ appearing close to each other in the solvent cage can immediately react with themselves. This reaction can occur with the participation of the ring or the nitrogen in radical β . If the ring is involved (reaction [8b]) then the transient products γ_i are formed. On the other hand, because of steric hindrance, reaction [8a] can only occur through an activated complex which dissociates to cation α and chloride ion after the electron transfer has taken place into the complex. Reaction of radical CCl₃ and radical β with simultaneous chlorine atom split off is another way that the nitrogen atom can be involved (reaction [10]).



Reaction [10], in which radical δ is formed, is supposedly more probable outside the solvent cage where the presence of chlorine atom acceptor or/and hydrogen atom donor facilitates its occurrence.

N-(Trichloroethylene)carbazole (2) found among the products of the photochemical reaction probably forms when radical δ reacts with radical CCl₃ following the pattern of reaction [11]. Because of steric hindrance, reaction of radicals δ and CCl₃ is only possible when accompanied by the cleavage of at least one C—Cl bond. So this reaction occurs when acceptor Cl or/and donor H is present.

In pure CCl_4 as well as in polar medium, product 2 forms with low yield. However, this compound is the main product of the reaction in 3-methylpentane non-polar medium which favours radical reactions. This fact supports the assumed radical mechanism of reactions [10] and [11]. In addition to reaction



[10], it has also been suggested that radical δ can be formed from cation α when electron donor is present (22).

Along with the possibilities of transformation of the carbazole radical cation in the solvent cage discussed above, the substitution reactions of the carbazole radical cation with chloride ion or chlorine atom probably take place in this reaction medium. Such reactions are suggested by the formation of chloroderivatives of carbazole. We have found 1-chlorocarbazole (3) among the products. Substitution reactions between aromatic radical cations and chloride ions are known in the literature (23). On the other hand, CCl_4 is the reaction medium in which chlorine atoms are easily generated (8, 19).



Carbon tetrachloride or trichloromethyl radical can be hydrogen acceptors while the chloride ions can serve as proton acceptors in reaction [12].

The carbon tetrachloride medium favours the chain photochemical reaction mechanism initiated by electron transfer from the electron donor to the CCl₄ molecule (16, 20, 24). The great photochemical activity of carbazole in CCl₄ can also be explained by chain reaction initiated by CCl₃ radicals in the presence of CCl₄. Comparatively low C—Cl bond energy in the CCl₄ molecule makes possible the participation of CCl₄ in the reaction as a hydrogen acceptor, the reaction scheme is as follows:



In the reaction above, the sum of bond energies undergoing splitting is smaller than the sum of energies of new bonds formed (14). Therefore reaction [13] might be an additional source of $Cl^-\gamma_i$ intermediates.

The reaction of CCl₃ radicals with α and γ_i cations in CCl₄ explains the formation mechanism of di-substituted transient products (reactions [14] to [19]).



The closing chain reaction might be

$$[20] \quad \mathbf{C} + \dot{\mathbf{C}}\mathbf{C}\mathbf{l}_3 \implies \boldsymbol{\beta} + \mathbf{C}\mathbf{H}\mathbf{C}\mathbf{l}_3$$

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$$\begin{array}{cccccccl} [23] & 2\dot{C}Cl_3 & \longrightarrow & C_2Cl_6 \\ & & 1 \end{array}$$

In pure CCl₄, ionic products α and γ_i can undergo further reactions with carbazole molecules resulting in the correspondingly α' and γ_i' monocations. The reaction scheme is as follows:





The mechanism proposed above for the photochemically initiated reaction in the carbazole $-CCl_4$ system has been strongly supported by a collection of data achieved while studying the reaction products. This will now be described more extensively.

Use of water after irradiation

If we add water to the photolysis solution, transient products, showing significant stability in pure CCl_4 , undergo easy hydrolysis resulting in corresponding (carbo-*N*-carbazyl)carbazole and carbazole – carboxylic acids (see Table 1).

The hydrolysis of intermediates α' and γ_i' partially explains the formation mechanism of N, N'-carbodicarbazyl (17), 1-(carbo-N-carbazyl)carbazole (18), and 3-(carbo-N-carbazyl)carbazole (19) according to the following scheme:



18, 19

Intermediates γ_i , being the precursors of carbazole-1-carboxylic acid (15), and carbazole-3-carboxylic acid (16), easily undergo further transformation in the presence of water until the proper acid chlorides [A], which are of intermediate character, are formed (reaction [28]), this transformation being followed by the formation of the acids (reaction [29]). The labile acid chlorides formed from intermediates γ_i can also undergo reaction with carbazole thus acting as additional source of products 18 and 19 (reaction [30]).





Intermediate α present in the reaction medium undergoing the reaction with water can give rise to not only mono-substituted but also to di-substituted (carbo-N-carbazyl)carbazoles. During the first step of the reaction, cation α undergoes transformation in the presence of water until N-(carbochloro)carbazole as an intermediate product [**B**] is formed (reaction [31]). Then [**B**] can undergo reaction with carbazole leading to the formation of **17** (reaction [33]) or **18** and **19** (reaction [34]). In the presence of water it should also undergo reaction resulting in the formation of unstable carbazole-N-carboxylic acid which presumably decomposes to carbazole and carbon dioxide (25), reaction [32].





Intermediate [B] formed in the reaction medium can also undergo reaction with products 17, 18, and 19 present, thus explaining the formation of 3,9di(carbo-N-carbazyl)carbazole (20), and 1,6-di-(carbo-N-carbazyl)carbazole (21), (reactions [35]– [37]). The formation of 1,3- and 3,6-di-substituted (carbo-N-carbazyl)carbazoles is less probable.

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The remaining part of carbazole present among the products of photolysis is efficiently used in reactions [30], [33], and [34]. This can be observed by TLC method.

Probably di-substituted (carbo-N-carbazyl)carbazoles can also be formed in another way. If intermediates α' and γ_i' , formed in the reactions [24] and [25] undergo reactions with the transient product α , these reactions lead to the corresponding di-cations, mainly to 1,6- and 3,9-di-substituted carbazole derivatives. These di-cations undergoing hydrolysis would explain the second way in which products 20 and 21 are formed. But it is presently difficult to estimate to what extent these reactions contribute to the formation of the above mentioned products.

Intermediate di-substituted monocations in the presence of water probably undergo transformations to proper carbazole – dicarboxylic acids. We did not manage to isolate these compounds.

Use of ethanol after irradiation

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If we add ethanol to the photolysis solution, the transient products formed in pure CCl₄ undergo reactions with alcohol, and mono- and di-substituted (carboethoxy)carbazoles are formed as a result. As ethanol contains traces of water, (carbo-N-carbazyl)carbazoles as well as carboxylic acids appear but with significantly lower yield than in the case when water is used (Table 1). In the reaction discussed there exists a probability of the participation of water from the surface of silica gel used as a filling of chromatographic column.

N-(carboethoxy)carbazole (4) appearing among

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the products when ethanol is added after irradiation, as well as N-cyanocarbazole found when the irradiated solution was saturated with ammonia gas (22) confirm the formation of transient α cation in the system of carbazole-CCl₄. The reaction mechanism between a cation and ethanol to give product 4 can be suggested as follows:



If intermediate α reacts first with an ethanol molecule (or two molecules) and then with the water molecule, the reaction results directly in 4 (reaction [38]), but when α reacts with the water molecule first, the transient product appearing in the reaction should be [B] which can undergo transformation in the presence of an excess of ethanol, mainly to 4 (reaction [39]). But when compared to the other products in this reaction, 4 is formed with relatively low yield.

Similar pattern exists for the reaction of transient products γ_i in the presence of ethanol during which 1-(carboethoxy)carbazole (5), 2-(carboethoxy)carbazole (6), 3-(carboethoxy)carbazole (7), and 4-(carboethoxy)carbazole (8) are formed (reactions [40] and [41]):

C₂H₅OH

<u>___</u>

$$[40] \quad Cl^{-}\gamma_{i} \xrightarrow{C_{2}H_{3}OH} (-HCl) \xrightarrow{H_{2}O} (-HCl) \xrightarrow{H_{2}O} (-2HCl) \xrightarrow{H_{2}O} (A] \xrightarrow{C_{2}H_{5}OH} (A] \xrightarrow{C_{2}H_{5}OH} (A) \xrightarrow{C_{2}H_{5}O$$

Products 5, 6, 7, and 8 confirm the existence of intermediates γ_i in the system carbazole-CCl₄ when irradiated. On the other hand di-substituted (carboethoxy)carbazoles: 3,9-di(carboethoxy)carbazole (9), 1,3-di(carboethoxy)carbazole (10), 1,6di(carboethoxy)carbazole (11), and 3,6-di(carboethoxy)carbazole (13) found among the products indicate that di-substituted cations are formed alongside with transient mono-substituted α and γ_i when the carbazole-CCl₄ system is irradiated. The probable mechanism of formation of di-substituted intermediates, as a result of the reactions between α and γ_i and CCl₃ radicals in the presence of CCl₄, was described by reactions [14] to [19].

The formation of 9, 10, 11, and 13 can be assessed as follows:



Use of ethanol as a solvent

When ethanol is used as a solvent of carbazole in the presence of CCl_4 , the secondary photochemical transformation is significantly changed in comparison with the reactions in pure CCl_4 described above.

The polar reaction medium favours the formation of ionic intermediates in the solvent cage which is supported by the products found in this reaction (Table 1).

Intermediates α and γ_i which have appeared

during irradiation can immediately undergo further reactions ([38] to [41]) which result in the formation of all the mono-substituted (carboethoxy)carbazoles. So, active participation of ethanol in the reaction medium probably eliminates reactions [14]–[19] leading to di-substituted cations. Furthermore, reactions of intermediates α and γ_i with carbazole molecules become less probable (reactions [24], [25]).

Attention should be paid to the fact that *N*-(carboethoxy)carbazole is formed with comparatively lower yield than 1-(carboethoxy)carbazole and 3-(carboethoxy)carbazole. This can be observed when TLC method is used. This fact suggests that the ethanol medium mainly favours the formation of intermediates γ_i which can be the result of both reactions [9] and [13]. When ethanolic solution of carbazole with CCl₄ was irradiated the mono(carboethoxy)carbazoles, formed during irradiation, also undergo photochemical reactions in the presence of CCl₄. This leads to di-substituted (carboethoxy)carbazoles, **9**, **10**, **11**, **12**, **13**, and **14** these being formed from the corresponding intermediate products (reaction [46]).



Reaction [46] can be used as a method of photochemical synthesis of di(carboethoxy)carbazoles.

The mechanism of one-electron photooxidation of carbazole in the presence of carbon tetrachloride already suggested by us in a recent paper (22) has been extended above and strongly supported by the qualitative study of the various reaction products obtained.

Fluorescence spectra

We are now in a good position to explain the new fluorescence emissions observed when ethanol solutions of carbazole in the presence of CCl_4 are irradiated (Fig. 1). We showed in Table 2 the wavelength of the maximum fluorescence intensity for a series of (carboethoxy)carbazoles. Obviously, the new fluorescence band at about 400 nm appearing in Fig. 1 during irradiation of the solution might be a complex mixture of the (carboethoxy)carbazole fluorescences. The spectroscopy and the

TABLE 2. Fluorescence maxima of a series of (carboethoxy)carbazole molecules in ethanol at room temperature excited at 320 nm

Molecules	$\lambda_{max}(F)$ (nm)
Carbazole	352
N-(Carboethoxy)carbazole	328 ($\lambda_{exc} = 310$)
1-(Carboethoxy)carbazole	397
2-(Carboethoxy)carbazole	404
3-(Carboethoxy)carbazole	362
4-(Carboethoxy)carbazole	430
3,9-Di(carboethoxy)carbazole	336
1,3-Di(carboethoxy)carbazole	398
1,6-Di(carboethoxy)carbazole	383
1,8-Di(carboethoxy)carbazole	372
3,6-Di(carboethoxy)carbazole	351
3,5-Di(carboethoxy)carbazole	400

photophysics of all these molecules are now being studied in our laboratory.

Experimental

Apparatus

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¹H-nmr spectra were 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 an AE1 MS902 mass spectrometer.

The absorption spectra were recorded on a Cary 14 spectrophotometer using a 10mm optical path cell. The emission spectra were recorded on a fluorescence spectrophotometer Model SF-1 "Fluorispec" (Baird-Atomic, INC; Cambridge, MA). All solutions examined in fluorescence were first degassed by the well-known freeze-thaw method.

Materials

Carbazole was an Eastman Organic chemical and was used without any further purification. Carbon tetrachloride from American Chemicals was of spectrograde quality and it was washed with a saturated sodium carbonate solution and then repeatedly with water, dried with calcium chloride and P₂O₅, and redistilled. Ethanol was purified by refluxing with concentrated sulfuric acid (4 mL H₂SO₄/1000 mL solvent) for 24 h and then was distilled twice before use.

Benzene and petroleum ether were distilled before use.

General procedure

Carbazole solutions (0.005 M) in pure CCl₄ or 0.1 M CCl₄ in ethanol were deoxygenated with oxygen-free argon and irradiated in a Pyrex Hanovia immersion-well reactor for 1 h with an Hanovia 679A36; 450 W medium-pressure mercury lamp. Hydrogen chloride generated during these reactions was neutralized with sodium carbonate. 1% sodium carbonate water solution or ethanol with sodium carbonate were added to the irradiated solution of carbazole in pure CCl₄. But only sodium carbonate was added to the irradiated carbazole solution with CCl₄ in ethanol. Solutions containing ethanol were mixed and then the sediment was separated by filtration. The remaining solutions were concentrated. The solution containing water (biphase system) was shaken, and then the CCl₄ was evaporated under vacuum. The remaining products not dissolved in water were precipitated at the bottom of the flask. Then water was decanted and products were dried using a stream of air.

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 and ethanol. Identified products have been listed in Table 1 and their $R_{\rm f}$ values on TLC plates with silica gel in Table 3.

Spectral characteristics of the photochemical products

Hexachloroethane (1): single crystals, unobserved by TLC. This compound is going down first on the chromatographic column. The product has been identified by comparison with the infrared and mass spectra of an authentic sample.

N-(*Trichloroethylene*)carbazole (2): was identified as described previously (22).

I-Chlorocarbazole (3): colorless crystalline solid; ¹H-nmr (CDCl₃) δ 7.09–7.53 (m, 5H, arom), 7.92, 8.01, 8.10 (3s, 2H, arom), 8.28 (s, 1H, N—H), (*d*₆-acetone) 7.10–7.70 (complex m, 5H, arom), 8.04–8.20 (m, 2H, arom), ~10.65 (s, broad band, 1H, N—H).

Infrared (film) \tilde{v}_{max} 3400 (s, N—H), 1620 (w), 1600 (m), 1555 (m), 1485 (m), 1445 (s), 1415 (s), 1360 (vw), 1325 (m), 1310 (m), 1260 (w), 1220 (w), 1200 (vw), 1175 (m), 1125 (m), 1020 (m), 920 (w), 845 (w), 790 (vw), 770 (w), 730 (vs) cm⁻¹.

Mass spectrum (70 eV) (mol wt for $C_{12}H_8NCl 201.66$), m/e 203 (M⁺, 33.7), 201 (M⁺, 100), 166 (42), 165 (29.4), 164 (26.2), 138 (42), 137 (11.7).

N-(*Carboethoxy*)*carbazole* (4): white crystalline solid; 'H-nmr (CDCl₃) δ 1.56 (t, J = 7 Hz, 3H, methyl), 4.60 (q, J = 7 Hz, 2H, methylene), 7.27–7.58 (m, 4H, arom), 7.94–8.04 (m, 2H, arom), 8.27–8.37 (m, 2H, arom).

Infrared (film) \bar{v}_{max} 3040–2830 (m), 1730 (vs, C=O), 1590 (w), 1480 (m), 1455 (m), 1440 (vs), 1420 (m), 1390 (s), 1365 (vs), 1335 (s), 1320 (vs), 1295 (vs), 1245 (s), 1215 (s), 1200 (vs), 1100 (s), 1040 (s), 1005 (m), 920 (m), 840 (m), 750 (vs), 740 (vs), 705 (s) cm⁻¹.

Mass spectrum (70 eV) (mol wt for $C_{15}H_{13}NO_2$ 239.28), *m/e* 239 (M⁺, 41.5), 180 (59.6), 167 (100), 166 (62.8), 140 (37.2), 139 (24.8).

I-(Carboethoxy)carbazole (5): white crystalline solid; ¹H-nmr (CDCl₃) δ 1.48 (t, J = 7 Hz, 3H, methyl), 4.50 (q, J = 7 Hz, 2H, methylene), 7.16–7.57 (m, 4H, arom), 8.05, 8.14, 8.22, 8.31 (2d, 3H, arom), 9.97 (s, 1H, N-H), (d_6 -acetone) 10.78 (s, broad band, 1H, N-H); ir and ms are the same as described previously (22).

2-(*Carboethoxy*)*carbazole* (6): white crystalline solid; ¹H-nmr (CDCl₃) δ 1.44 (t, J = 7 Hz, 3H, methyl), 4.43 (q, J = 7 Hz, 2H, methylene), 7.21–7.50 and 7.90–8.20 (2m, 3H and 4H, arom), 8.25 (s, 1H, N—H), (d_{e} -acetone) 10.63 (s, 1H, N—H).

Infrared (film) \tilde{v}_{max} 3400 (s, N—H), 1685 (vs, C=O), 1620 (s), 1490 (w), 1450 (m), 1435 (s), 1375 (w), 1350 (w), 1330 (m), 1315 (w), 1285 (m), 1260 (m), 1210 (m), 1080 (w), 1015 (w), 980 (vw), 860 (m), 825 (w), 810 (vw), 760 (vw), 735 (vs), 710 (s) cm⁻¹.

Mass spectrum (70 eV) (mol wt for $C_{15}H_{13}NO_2$ 239.28), *m/e* 239 (M⁺, 100), 211 (28.7), 194 (72), 166 (39.3), 139 (22.3).

3-(Carboethoxy)carbazole (7): white crystalline solid; ¹H-nmr (CDCl₃) δ 1.45 (t, J = 7 Hz, 3H, methyl), 4.44 (q, J = 7 Hz, 2H, methylene), 7.18–7.48 (m, 4H, arom), 8.08, 8.18 (2s, 2H, arom), 8.82 (s, 1H, arom), 8.41 (s, 1H, N—H), (d_6 -acetone) 10.74 (s, broad band, 1H, N—H); ir and ms are the same as described previously (22).

4-(Carboethoxy)carbazole (8): white crystalline solid; ¹H-nmr (CDCl₃) δ 1.49 (t, J = 7 Hz, 3H, methyl), 4.54 (q, J = 7 Hz, 2H, methylene), 7.19–7.93 (complex m, 6H, arom), 8.82, 8.91 (2s, 1H, arom), 8.30 (s, 1H, N—H), (d_6 -acetone) ~10.73 (s, 1H, N—H).

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		De	veloping s	system† (v/	v)		
			PE-EE				
No.*	PE	100:1	20:1	5:1	В	10:1	в-е 2:1
С	0.03	0.05	0.13	0.40	0.76	0.80	
2	0.68	0.76	0.82	0.88	0.89	0.90	
3	0.18	0.26	0.42	0.70	0.82	0.86	
4	0.06	0.24	0.52	0.77	0.75	0.85	
5	0.03	0.10	0.28	0.54	0.67	0.80	
6			0.02	0.08	0.23	0.48	
7			0.03	0.11	0.27	0.54	
8			0.05	0.20	0.49	0.70	
9		0.03	0.14	0.42	0.45	0.82	
10			0.06	0.25	0.40	0.75	
11				0.13	0.19	0.59	
12		0.06	0.23	0.61	0.45	0.84	
13					0.05	0.25	
14					0.06	0.29	
15							0.20
16							0.28
17	0.07	0.23	0.50	0.73	0.83	0.87	
18		0.06	0.12	0.41	0.73	0.84	
19				0.04	0.29	0.51	
20			0.07	0.33	0.69	0.87	
21				0.06	0.47	0.75	

TABLE 3. $R_{\rm f}$ values of the photoproducts in the carbazole-CCl₄ system

*Notation of compounds is the same as in Table 1. †B: benzene; PE: petroleum ether; E: ethanol; EE: ethyl ether.

Infrared (Nujol film) v_{max} 3350 (s, N-H), 1690 (vs, C=O) 1590 (m), 1430 (m), 1395 (m), 1360 (m), 1330 (w), 1320 (m), 1305 (vs), 1285 (m), 1270 (vs), 1225 (w), 1180 (s), 1150 (m), 1135 (s), 1110 (m), 1085 (m), 1020 (m), 1010 (m), 745 (s), 730 (m), 720 (vs) cm⁻¹.

Mass spectrum (70 eV) (mol wt for C₁₅H₁₃NO₂ 239.28), m/e 239 (M⁺, 100), 211 (23.7), 195 (10.7), 194 (63.7), 193 (2.2), 167 (19.7), 166 (41.4), 165 (9.1), 164 (5.7), 139 (21.4).

3,9-Di(carboethoxy)carbazole (9): white crystalline solid; ¹H-nmr (CDCl₃) δ 1.45 and 1.57 (2t, J = 7 Hz, 6H, methyl), 4.44 and 4.62 (2q, J = 7 Hz, 4H, methylene), 7.25-7.65 and <math>8.0-8.45(2m, 2H, and 4H, arom), 8.67 (s, 1H, arom).

Infrared (film) v_{max} 1730 (vs, C=O), 1695 (vs, C=O), 1610 (w), 1585 (m), 1475 (m), 1440 (s), 1420 (s), 1380 (w), 1360 (s), 1330 (m), 1310 (m), 1295 (m), 1275 (w), 1230 (vs), 1190 (s), 1090 (s), 1040 (m), 1010 (s), 915 (w), 885 (w), 760 (m), 745 (m), 730 (m), 700 (m) cm⁻¹

Mass spectrum (70 eV) (mol wt for $C_{18}H_{17}NO_4$ 311.34), m/e 311 (M⁺, 50.3), 266 (11.7), 239 (29.1), 238 (25.9), 210 (13.5), 194 (100), 193 (25.8), 167 (27.7), 166 (48.2), 165 (40.4), 164 (31.2), 139 (33.3), 138 (26.9).

1,3-Di(carboethoxy)carbazole (10): white crystalline solid; ¹H-nmr (CDCl₃) δ 1.47 and 1.49 (2t, J = 7 Hz, 6H, methyl), 4.46 and 4.51 (2q, J = 7 Hz, 4H, methylene), 7.20-7.60 (m, 3H, arom), 8.10, 8.18 (2s, 1H, arom), 8.78 (d, J = 1.8 Hz, 1H, arom), 8.98 (s, 1H, arom), 10.16 (s, 1H, N--H), (d₆-acetone) 11.16 (s, 1H, N-H).

Infrared (Nujol film) \tilde{v}_{max} 3360 and 3320 (s, N—H), 1695 (s, C=O), 1670 (vs, C=O), 1620 (vw), 1595 (s), 1565 (w), 1385 (m), 1355 (m), 1325 (s), 1305 (s), 1260 (vs), 1230 (s), 1210 (s), 1200 (s), 1180 (s), 1140 (w), 1110 (w), 1090 (m), 1060 (s), 1015 (m), 1000 (w), 900 (w), 780 (w), 760 (m), 715 (s) cm⁻¹.

Mass spectrum (70 eV) (mol wt for C₁₈H₁₇NO₄ 311.34), m/e

311 (M⁺, 65.3), 267 (3.8), 266 (27.5), 265 (100), 239 (1.5), 238 (7.6), 237 (16.2), 220 (2.9), 210 (3), 294 (1), 293 (5), 292 (8.4), 165 (7.6), 164 (12.3), 44 (8.8).

1,6-Di(carboethoxy)carbazole (11): white crystalline solid; ¹H-nmr (CDCl₃) δ 1.44 and 1.47 (2t, J = 7 Hz, 6H, methyl), 4.42 and 4.44 (2q, J = 7 Hz, 4H, methylene), 7.25–7.60 and 8.05–8.40 (2 complexes m, 5H, arom), 8.82 (d, J = 1.8 Hz, 1H, arom).

Infrared (Nujol film) \tilde{v}_{max} 3370 (s, N—H), 1700 (s, C=O) 1670 (s, C=O), 1615 (w), 1595 (s), 1490 (m), 1415 (m), 1355 (m), 1335 (m), 1300 (s), 1260 (vs), 1245 (vs), 1215 (s), 1200 (s), 1180 (m), 1145 (s), 1115 (m), 1100 (vs), 1060 (m), 1020 (m), 755 (m), 735 (m), 715 (m) cm⁻¹

Mass spectrum (70 eV) (mol wt for C₁₈H₁₇NO₄ 311.34), m/e (M⁺, 100), 267 (8.4), 266 (43.7), 265 (99.7), 239 (2.5), 238 (7.5), 237 (13.5), 220 (44.7), 210 (3.2), 194 (3.7), 193 (16), 192 (17.5), 165 (8.8), 164 (28), 44 (14.3).

1,8-Di(carboethoxy)carbazole (12): white crystalline solid. Infrared (film) \bar{v}_{max} 3410 (w, N—H), 2950–2820 (s), 1685 (s C=O), 1595 (m), 1490 (m), 1465 (m), 1450 (w), 1425 (m), 1360 (m), 1290 (w), 1265 (vs), 1200 (vs), 1160 (m), 1140 (vs), 1080 (m), 1010 (w), 740 (m), 715 (m) cm⁻¹.

Mass spectrum (70 eV) (mol wt for C₁₈H₁₇NO₄ 311.34), m/e 311 (M⁺, 100), 296 (22.2), 267 (9.5), 266 (16.6), 265 (14), 220 (19), 194 (23.3), 193 (79), 192 (16.4), 165 (14.4), 164 (28.2)

3,6-Di(carboethoxy)carbazole (13): white crystalline solid; ¹H-nmr (CDCl₃) δ 1.45 (t, J = 7 Hz, 6H, methyl), 4.44 (q, J =7 Hz, 4H, methylene), 7.41 and 7.50 (2s, 2H, arom), 8.13 and 8.23 (2d, J = 1.8 Hz, 2H, arom), 8.87 (d, J = 1.8 Hz, 2H, arom), 8.49 (s, 1H, N-H).

Infrared (Nujol film) \bar{v}_{max} 3300 (s, N—H), 1685 (vs, C=O), 1615 (w), 1595 (w), 1350 (m), 1300 (m), 1280 (m), 1260 (s), 1225 (m), 1210 (m), 1090 (m), 1015 (m), 755 (m), 710 (s) cm⁻¹.

Mass spectrum (70 eV) (mol wt for C₁₈H₁₇NO₄ 311.34), m/e

311 (M^+ , 100), 267 (10.3), 266 (65.9), 265 (1.3), 239 (5.2), 238 (26.8), 237 (2.1), 210 (10.9), 194 (3.3), 193 (12.4), 192 (4.4), 165 (6.8), 164 (11.1), 44 (14).

3,5-Di(carboethoxy)carbazole (14): white crystalline solid; ¹H-nmr (CDCl₃) δ 1.52 and 1.54 (2t, J = 7 Hz, 6H, methyl), 4.43 and 4.52 (2q, J = 7 Hz, 4H, methylene), 7.15–8.55 (complex m, 5H, arom), 9.54 (s, 1H, arom).

Infrared (film) \tilde{v}_{max} 3260 (s, N—H), 2950–2800 (s), 1700 (vs, C=O), 1675 (vs, C=O), 1605 (s), 1595 (s), 1555 (w), 1440 (w), 1390 (w), 1375 (w), 1355 (m), 1310 (s), 1280 (s), 1270 (s), 1240 (vs), 1160 (s), 1140 (m), 1125 (m), 1100 (m), 1015 (m), 755 (w), 735 (m), 710 (m) cm⁻¹.

Mass spectrum (70 eV) (mol wt for $C_{18}H_{17}NO_4$ 311.34), m/e 311 (M⁺, 100), 267 (12.7), 266 (68.8), 265 (0.8), 239 (6.1), 238 (23.8), 237 (1.4), 210 (6.0), 194 (6.4), 193 (14.7), 192 (17.5), 165 (10.4), 164 (13.7), 44 (15.5).

Carbazole-1-carboxylic acid (15): white crystalline solid; 'H-nmr (CDCl₃) δ 7.26–7.55 (m, 4H, arom), 8.07–8.38 (m, 3H, arom), ~9.92 (s, 1H, N—H); (d,-acetone) 10.76 (s, 1H, N—H).

arom), ~9.92 (s, 1H, N—H); (d_6 -acetone) 10.76 (s, 1H, N—H). Infrared (film) \tilde{v}_{max} 3395 (s, N—H), 1660 (s, C=O), 1610 (m), 1590 (m), 1480 (m), 1420 (s), 1300 (s), 1250 (m), 1215 (m), 1200 (m), 1130 (m), 1100 (m), 1055 (w), 1010 (w), 915 (w), 850 (w), 810 (w), 745 (vs), 715 (s) cm⁻¹.

Mass spectrum (70 eV) (mol wt for $C_{13}H_9NO_2$ 211.22), *m/e* 211 (M⁺, 52.5), 194 (19.8), 193 (100), 166 (17.7), 165 (69.5), 139 (18.4), 138 (19.5).

Carbazole-3-carboxylic acid (16): white crystalline solid; ¹H-nmr (CDCl₃) δ 7.20–7.55 (m, 4H, arom), 8.11 and 8.15, 8.25 (s, s, and 2d, J = 1.8 Hz, 2H, arom), 8.90 (s, 1H, arom), 8.38 (s, 1H, N—H).

Infrared (film) \tilde{v}_{max} 3375 (m, N—H), 1665 (vs, C==O), 1615 (m), 1595 (vs), 1570 (m), 1480 (m), 1435 (m), 1400 (s), 1320 (s), 1295 (m), 1260 (s), 1230 (s), 1210 (m), 1190 (m), 1120 (m), 1010 (w), 920 (w), 900 (w), 810 (w), 765 (m), 750 (m), 735 (m), 710 (s) cm⁻¹.

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Mass spectrum (70 eV) (mol wt for $C_{13}H_9NO_2$ 211.22), m/e 211 (M⁺, 100), 194 (48.2), 193 (47.8), 166 (36.2), 165 (39.0), 164 (25.2), 139 (30.5), 138 (14.2).

N,N'-Carbodicarbazyl (17): white crystalline solid; 'H-nmr $(CDCl_3) \delta 7.26-7.42 (m, 12H, arom), 8.0-8.14 (m, 4H, arom).$

Infrared (film) \tilde{v}_{max} 1695 (vs, C=O), 1590 (w), 1470 (m), 1445 (s), 1430 (m), 1365 (s), 1335 (w), 1320 (s), 1300 (m), 1290 (s), 1230 (w), 1205 (s), 1170 (m), 1145 (m), 1110 (w), 1090 (w), 1020 (w), 925 (w), 825 (m), 760 (w), 740 (vs), 710 (s) cm⁻¹.

Mass spectrum (70 eV) (mol wt for $C_{25}H_{16}N_2O$ 360.42), *m/e* 360 (M⁺, 17.0), 194 (46.8), 166 (100), 140 (23.4), 139 (11.3).

l-(*Carbo*-N-*carbazyl*)*carbazole* (18): white crystalline solid; ¹H-nmr (CDCl₃) δ 7.12–7.45 and 7.49–7.79 (2 complexes m, 10H, arom), 8.01–8.22 (m, 4H, arom), 8.31, 8.39 (2s, 1H, arom), 9.75 (s, 1H, N—H), (d_6 -acetone) 7.22–7.78 (complex m, 11H, arom), 8.11–8.33 (m, 3H, arom), 8.46, 8.55 (2s, 1H, arom), 10.91 (s, 1H, N—H).

Infrared (film) \tilde{v}_{max} 3420 (m, N—H), 1650 (s, C=O), 1615 (w), 1595 (m), 1480 (m), 1470 (m), 1445 (s), 1435 (s), 1420 (m), 1350 (m), 1320 (s), 1310 (s), 1290 (s), 1270 (s), 1250 (w), 1210 (s), 1165 (w), 1145 (m), 1130 (m), 1105 (m), 1090 (m), 1055 (w), 945 (w), 920 (w), 830 (w), 800 (w), 770 (m), 740 (vs), 710 (s) cm⁻¹.

Mass spectrum (70 eV) (mol wt for $C_{25}H_{16}N_2O$ 360.42), m/e 360 (M⁺, 10.6), 194 (100), 166 (78.7), 139 (51).

3-(Carbo-N-carbazyl)carbazole (19): white crystalline solid; ¹H-nmr (CDCl₃) δ 7.24–8.13 (complex m, 14H, arom), 8.55 (s, 1H, arom), 8.40 (s, 1H, N—H), (d₆-acetone) 7.14–7.90 (m, 11H, arom), 8.10–8.27 (m, 3H, arom), 8.64 (s, 1H, arom), 10.91 (s, 1H, N—H).

Infrared (Nujoi film) \bar{v}_{max} 3400 (m, N—H), 1660 (s, C=O), 1620 (w), 1595 (m), 1570 (w), 1465 (m), 1435 (s), 1350 (s), 1320 (s),

1300 (m), 1275 (m), 1240 (m), 1220 (m), 1210 (m), 1185 (w), 1140 (m), 1120 (m), 1055 (w), 1010 (w), 930 (w), 840 (w), 815 (m), 760 (w), 745 (s), 710 (s) cm⁻¹.

Mass spectrum (70 eV) (mol wt for $C_{25}H_{16}N_2O$ 360.42), m/e 360 (M⁺, 8.5), 194 (100), 166 (31.9), 139 (22).

3,9-Di(carbo-N-carbazyl)carbazole (20): white crystalline solid; ¹H-nmr (CDCl₃) δ 7.26–7.65 (complex m, 16H, arom), 7.92–8.12 (m, 6H, arom), 8.54 (s, 1H, arom).

Infrared (Nujol film) \bar{v}_{max} 1700 (vs, C=O), 1670 (s, C=O), 1615 (w), 1595 (m), 1435 (vs), 1350 (s), 1330 (w), 1315 (vs), 1290 (vs), 1275 (m), 1235 (m), 1220 (m), 1205 (s), 1190 (w), 1165 (m), 1145 (m), 1110 (w), 1090 (w), 1075 (w), 1020 (m), 915 (w), 885 (w), 870 (w), 820 (m), 765 (m), 740 (vs), 710 (s) cm⁻¹.

Mass spectrum (70 eV) (mol wt for $C_{38}H_{23}N_3O_2$ 553.63), *m/e* 553 (M⁺, 11.2), 387 (95.0), 194 (26.7), 167 (23.3), 166 (100), 165 (20.8), 164 (13.3), 140 (12.5), 139 (10), 138 (6.7).

1,6-Di(carbo-N-carbazyl)carbazole (21): white crystalline solid; 'H-nmr (CDCl₃) δ 7.14–7.82 (complex m, 15H, arom), 7.94–8.22 (m, 5H, arom), 8.35, 8.42 (2s, 1H, arom), 8.51 (s, 1H, arom), 9.87 (s, 1H, N—H), (d_6 -acetone) 11.01 (s, 1H, N—H).

Infrared (film) \tilde{v}_{max} 3410 (m, N—H), 1670 (vs, C=O), 1660 (vs, C=O), 1615 (m), 1595 (s), 1570 (m), 1485 (s), 1475 (s), 1445 (vs), 1435 (vs), 1420 (s), 1345 (s), 1315 (vs), 1290 (vs), 1270 (vs), 1250 (w), 1235 (w), 1210 (vs), 1170 (w), 1140 (s), 1120 (m), 1105 (m), 1095 (m), 1055 (m), 1020 (w), 940 (w), 925 (vw), 895 (vw), 860 (vw), 830 (w), 815 (vw), 795 (w), 780 (w), 745 (vs), 710 (s) cm^{-1}.

Mass spectrum (70 eV) (mol wt for $C_{38}H_{23}N_3O_2$ 553.63), *m/e* 553 (M⁺, 5.7), 387 (41.7), 194 (100), 193 (10), 166 (45.8), 165 (20), 164 (10.8), 140 (10), 139 (24.2), 138 (5).

Conclusion

The following scheme describes the complex mechanism of photochemical reactions in the carbazole- CCl_4 system in pure CCl_4 as well as in ethanol as the reaction media:

 $(C^{\delta^+} \cdots CCl_4^{\delta^-})^* \rightarrow [C^+ Cl^- CCl_3] \rightarrow \alpha, \beta, and \gamma_i \rightarrow products$

The electron transfer from the electronically excited carbazole molecule to CCl_4 molecule in the excited CT complex is the primary photochemical reaction followed by the primary photoproducts in the solvent cage. The radical cation of carbazole undergoes transformations in the presence of chloride ion and trichloromethyl radical in the solvent cage giving radical β and cations α and γ_i . Following that, depending upon the reaction media used, intermediates α , β , and γ_i undergo further transformation to proper thermodynamically stable products. This mechanism of one-electron photooxidation of carbazole in the presence of carbon tetrachloride was strongly supported by a qualitative study of the various reaction products obtained.

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- 1. А. Анмаd and G. DUROCHER. Can. J. Spectrosc. 26(1), 19 (1981).
- A. AHMAD and G. DUROCHER. Photochem. Photobiol. 34, 573 (1981).
- G. LESSARD and G. DUROCHER. Can. J. Spectrosc. 23, 130 (1978); J. Phys. Chem. 82, 2812 (1978); Photochem. Photobiol. 29, 399 (1979).
- 4. W. R. WARE and C. LEWIS. J. Chem. Phys. 57, 3546 (1972).
- R. O. LOUFTY and A. C. SOMERSALL. Can. J. Chem. 54, 760 (1976).
- 6. J. KLEIN, V. P. PLAZANET, and G. LAUSTRIAT. J. Chim. Phys. 67, 302 (1970); J. KLEIN and G. LAUSTRIAT. J. Chim. Phys. 67, 310 (1970).
- 7. D. SAPERSTEIN and E. LEVIN. J. Chem. Phys. 62, 3560 (1975).
- 8. J. R. BEWS and CH. GLIDEWELL. J. Mol. Struct. 71, 287 (1981).
- 9. V. I. SKVORTSOV and M. V. ALFIMOV. Opt. Spectrosc. 41, 284 (1976).
- M. BAILLET and G. DUROCHER. J. Phys. Chem. To be published; R. SOLARO, E. CHIELLINI, and A. LEDWITH. J. Chem. Soc. Chem. Commun. 580 (1980); 583 (1980); U. LANDMAN, A. LEDWITH, D. G. MARSCH, and D. J. WILLIAMS. Macromolecules, 9, 833 (1976); L. P. ELLINGER. Advances in macromolecular chemistry. Vol. 1. Edited by W. M. Pasika, Academic Press, NY. 1968. p. 169.
- 11. I. FISCHER-HJALMARS and M. SUNDBOM. Acta Chem. Scand. 22, 607 (1968).

- 12. J. F. AMBROSE and R. F. NELSON. J. Electrochem. Soc. 115, 1159 (1968).
- 13. J. F. AMBROSE, L. L. CARPENTER, and R. F. NELSON, J. Electrochem. Soc. 122, 876 (1975).
- S. L. MUROV. Handbook of photochemistry. Marcel Dekker, Inc., New York. 1973.
- 15. E. J. LAND. Prog. React. Kinet. 3, 371 (1965).
- T. LATOWSKI and B. ZELENT. ROCZ. Chem. 48, 831 (1974);
 51, 1883 (1977).
- 17. T. LATOWSKI and K. WYRZYKOWSKA. Rocz. Chem. 49, 833 (1974).
- K. WYRZYKOWSKA, M. GRODOWSKI, K. WEISS, and T. LATOWSKI. Photochem. Photobiol. 28, 311 (1978).
- T. IWASAKI, T. SAWADA, M. OKUYAMA, and H. KAMADA.
 J. Phys. Chem. 82, 371 (1978); Photographic Sci. Eng. 22, 312 (1978).
- 20. T. LATOWSKI and B. ZELENT. J. Org. Chem. 20, 3559 (1979).
- A. LEDWITH and M. SAMBHI. J. Chem. Soc. Chem. Commun. 64 (1965); V. A. BOROVKOVA, KH. S. BAGDA-SAR'YAN, V. F. PIKEL'NI, V. A. KOLOSOV, and YU. I. KIRYUKHIN. Dokl. Adad. Nauk SSSR, 224(3), 616 (1975).
- 22. B. ZELENT and G. DUROCHER. J. Org. Chem. 46, 1496 (1981).
- 23. A. J. BARD, A. LEDWITH, and H. J. SHINE. Adv. Phys. Org. Chem. 13, 155 (1976).
- 24. T. LATOWSKI and E. SIKORSKA. Rocz. Chem. 42, 1063 (1968).
- 25. J. MARCH. Advanced organic chemistry. McGraw-Hill Book Company, 1977. p. 807.