

PHOTOCHEMICAL REACTION OF CARBAZOLE AND SOME DERIVATIVES IN DICHLOROMETHANE

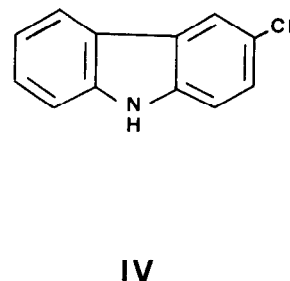
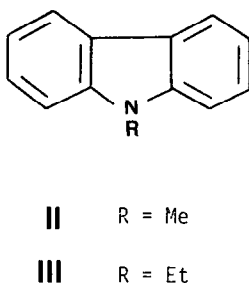
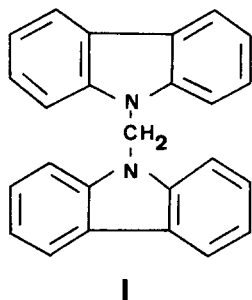
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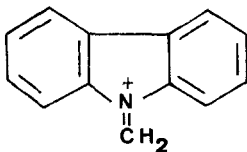
Abstract: By irradiation of carbazole and some derivatives in  $\text{CH}_2\text{Cl}_2$  soln two different reaction pathways were observed depending on the substitution of the heterocyclic compound.

Our interest in the photochemical reactions of nitrogen heterocyclic compounds<sup>1</sup> prompted us to investigate the photochemical behavior of carbazole and some derivatives in dichloromethane solution.<sup>2</sup>

The UV irradiation of carbazole in  $\text{CH}_2\text{Cl}_2$  soln gave a mixture of several products from which we were able to separate and to identify the thermodynamically stable products I-IV<sup>4</sup> (For Experimental Conditions see Note 3).



There is no doubt that this photoreaction may be due to the electronic excited carbazole molecule -  $\text{CH}_2\text{Cl}_2$  molecule interaction. Thus, the excited charge transfer complex (exciplex)<sup>5</sup> formed gives the carbazolyl radical cation:  $(\text{CARB}^{\delta+} \dots \text{CH}_2\text{Cl}_2^{\delta-} \leftrightarrow \text{CARB}^+ \dots \text{Cl}^- \dots \cdot\text{CH}_2\text{Cl})^* \rightarrow (\text{CARB}^+ \cdot \text{Cl}^- \cdot \text{CH}_2\text{Cl})$ . In the solvent cage this radical cation reacts, under its more likely mesomeric structures (9 and 3) with  $\cdot\text{CH}_2\text{Cl}$  and  $\text{Cl}^-$  to give cation A<sup>6</sup> and compound IV respectively. Cation A could be the source of I, II and III. In the reaction media  $\text{Cl}^-$  and  $(\text{Cl}_2\text{CH})_2$  were also detected.<sup>3</sup>  $(\text{Cl}_2\text{CH})_2$  derives from the dimerization of  $\text{Cl}_2\dot{\text{C}}\text{H}$ , which could be formed by hydrogen abstraction from  $\text{CH}_2\text{Cl}_2$  during the formation of II and III.

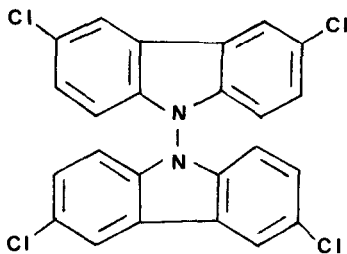


A

The same photochemical procedure was then applied to 3-chlorocarbazole giving products derived from an excited CT complex too.

Undoubtedly, the excited substrate (donor) - solvent (acceptor) interaction plays a very important role in the electron transfer phenomenon which only occurs under certain conditions. As it is known<sup>7</sup>, this interaction decreases from  $\text{CCl}_4$  to  $\text{CH}_2\text{Cl}_2$  and as carbazole is a weak base we thought that the interaction could be inhibited by appropriate electron acceptor substituents. According to this, we irradiated 3,6-dichlorocarbazole in  $\text{CH}_2\text{Cl}_2$  soln. The irradiation performed in a similar manner afforded the 9,9'-bis(3,6-dichlorocarbazyl) (V) as the only product; its physical and spectroscopical properties agree with a dimeric structure.<sup>8</sup>

The same photodimerization was observed in the case of the 3,6-dibromo derivative.

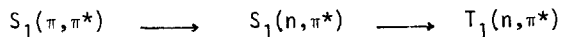


V

It is noteworthy that the photodimerization occurs through a different mechanism from that already discussed. In our opinion the excited 3,6-dichlorocarbazole is not able to form an exciplex with a  $\text{CH}_2\text{Cl}_2$  molecule and, after the photon absorption, hydrogen elimination occurs and a 9-aminy radical (9-(3,6-dichlorocarbazyl) radical) is formed. This photochemical behavior is similar to that described by us for 9H-pyrido(3,4-b)indoles.<sup>1</sup>

As it can be seen, the photochemical reaction pathway depends on the nature of the substituents present in the carbazole ring. It is interesting to mention that both reactions (excited CT complex formation and radical dimerization) are not concurrent, at least, in any of the examples studied by us.

From the photochemical point of view after the UV absorption by carbazole an  $S_1(\pi, \pi^*)$  state is reached.<sup>9</sup> This excited state forms with a  $\text{CH}_2\text{Cl}_2$  molecule the mentioned exciplex beginning the series of reactions already discussed. On the other hand, due to the higher electron affinity of 3,6-dichlorocarbazole the interaction with the solvent does not take place and the following sequence occurs:



From the last state an aminyl radical could be formed through the homolytic fission of the NH bond. The  $T_1(n,\pi^*)$  nature of the photoreactive state was also made evident because the photo reaction was inhibited in  $\text{AcOH}^1$  and  $\text{EtOH}^1$  media. Another result that supports the radical character of this reaction is the oxidation with  $\text{KMnO}_4$ . Thus, the product V was also obtained when 3,6-dichlorocarbazole was treated with this reagent under neutral conditions and as it is known<sup>10</sup> this reaction occurs by a radical mechanism.

The same photodimerization was observed when  $\text{CCl}_4$  was used as a solvent although its electron affinity is higher than that of  $\text{CH}_2\text{Cl}_2$ .

To confirm that 9-aminy radicals could be formed through the postulated pathway without involving an exciplex we submitted carbazole to UV irradiation in petroleum ether. In agreement with our assumption only the dimer 9,9'-biscarbazy<sup>11</sup> (VI) was detected.

Studies on the scope of these reactions are being carried out in our laboratory.

Acknowledgement: We thank UMYMFOR (CONICET-FCEyN-UBA) for the spectroscopic measurements and for microanalyses.

#### References and Notes

1. R. Erra Balsells and A.R. Frasca, Tetrahedron **39**, 33-39 (1983).
2. Carbazole was previously irradiated by B. Zelent and G. Durocher (J. Org. Chem. **46**, 1496 (1981)). They found that the main products obtained from the photochemical reaction of carbazole with  $\text{CCl}_4$  in  $\text{EtOH}$  as a solvent were 1-(carboethoxy)carbazole and 3-(carboethoxy)carbazole whereas in 3-methylpentane solution N-(trichloroethylene)carbazole was obtained.
3. Experimental Conditions. The carbazoles (100 mg) were irradiated in  $\text{CH}_2\text{Cl}_2$  solns (100 ml) in quartz Erlenmeyer flasks (125 ml) with stirring. The light source was a high-pressure Hg lamp (Hanau-Quarzlampen G.m.b.H, TQ 150) which was placed 10 cm from the flasks and the irradiation time was 18h.  
The residue obtained by evaporation of the solvent was chromatographed on a neutral aluminum oxide column. Benzene and benzene-petroleum ether mixtures were used as eluents. The products obtained were identified from their m.p.; U.V.; I.R.; M.S.;  $^1\text{H-NMR}$  and GC/M.S. (carried out on a column of 3% OV-101, 6 ft x 1,6 mm; on 60-80 mesh diatomite W). The  $\text{Cl}^-$  and  $(\text{Cl}_2\text{CH})_2$  were characterized by the  $\text{AgNO}_3/\text{HNO}_3$  test and by GC/M.S. (carried out on a PORAPAK-Q column, 4 ft x 2 mm on 80-100 mesh) respectively.  
Irradiations in other solvents were performed in a similar manner.
4. bis(9-Carbazy)l methane (I) (yield 10%), colorless needles from benzene, m.p. 290-291°.  $^1\text{H-NMR}$  (100 MHz;  $\text{DMSO-d}_6$ ; TMS)  $\delta$   $\text{H}_4\text{-H}_5$  and  $\text{H}_4\text{'-H}_5\text{'}$ , 8.18 (d, J 8 Hz);  $\text{H}_1$ ,  $\text{H}_8$  and  $\text{H}_{1\text{'}}$ ,  $\text{H}_{8\text{'}}$ , 7.66 (d, J 8 Hz);  $\text{H}_2\text{-H}_3$ ,  $\text{H}_6\text{-H}_7$  and  $\text{H}_{2\text{'}}$ ,  $\text{H}_{3\text{'}}$ ,  $\text{H}_{6\text{'}}$ ,  $\text{H}_{7\text{'}}$ , 7.29 (m);  $\text{CH}_2$  7.12 (s).  
M.S. m/z(%) 347(7); 346( $\text{M}^+$ , 28); 181(14); 180(100); 179(10); 178(6); 173(12); 167(23); 166(10); 152(17); 151(6); 140(10); 139(8); 73(6); 63(5); 51(5); 44(7).  
9-Methylcarbazole (II) (yield 3%), 9-ethylcarbazole (III) (yield 2%) and 3-chlorocarbazole (IV) (yield 35%) have been previously recorded in the literature (T.S. Stevens and S.H. Tucker, J. Chem. Soc. **123**, 2140 (1923) and G. Mazzara and M. Lamberti-Zanardi, Gazz. Chim. Italiana **26**, 236 (1896)) and they were characterized by their m.p., M.S. and  $^1\text{H-NMR}$  spectra.
5. A.J. Bard, A. Ledwith and H.J. Shine, Advances in Phys. Org. Chem. **13**, 155 (1976).

6. It is noteworthy that the M.S. of I, II and III show a very important peak at  $m/z$  180, corresponding to the cation A. It would indicate that this is a very stable structure.
7. J. Klein, V.P. Plazanet and G. Laustriat, J. Chim. Phys. **67**, 302 (1970).
8. 9,9'-bis(3,6-dichlorocarbazy) (V) (yield 12%), colorless plates from benzene-EtOH, m.p. 240-242° (lit 243-245°, G. Mazzara and M. Lamberti-Zanardi, Gazz. Chim. Italiana **26**, 236 (1896)).  
 $^1\text{H-NMR}$  (100 MHz;  $\text{DMSO-d}_6$ ; TMS)  $\delta$   $\text{H}_4\text{-H}_5$  and  $\text{H}_{4'}\text{-H}_{5'}$ , 8.59 (d, J 2 Hz);  $\text{H}_2$ ,  $\text{H}_7$  and  $\text{H}_{2'}$ ,  $\text{H}_{7'}$ , 7.45 (dd, J 2 and 8 Hz);  $\text{H}_1$ ,  $\text{H}_8$  and  $\text{H}_{1'}$ ,  $\text{H}_{8'}$ , 6.95 (d, J 8 Hz).  
M.S.  $m/z(\%)$  472(12); 471(6); 470(24); 468(19); 238(20); 237(20); 236(92); 235(33); 234(100); 200(10); 199(8); 198(12); 164(28); 84(21); 66(28).
9. G. Favini and A. Gamba, Gazz. Chim. Italiana 627 (1968).
10. H.J. Rosenkranz, B. Winkler-Lardelli, H.J. Hansen and H. Schmid, Helv. Chim. Acta **57**, 887 (1974).
11. 9,9-bisCarbazy (VI) (yield 10%), colorless plates from benzene, m.p. 224-225° (lit 225°; W.H. Perkin Jr. and S.H. Tucker, J. Chem. Soc. 119 (1921)).  
 $^1\text{H-NMR}$  (100 MHz;  $\text{Cl}_3\text{CD}$ ; TMS)  $\delta$   $\text{H}_4\text{-H}_5$  and  $\text{H}_{4'}\text{-H}_{5'}$ , 8.17 (dd, J 2 and 8 Hz);  $\text{H}_2\text{-H}_3$ ,  $\text{H}_6\text{-H}_7$  and  $\text{H}_{2'}\text{-H}_{3'}$ ,  $\text{H}_{6'}\text{-H}_{7'}$ , 7.29 (m);  $\text{H}_1$ ,  $\text{H}_8$  and  $\text{H}_{1'}$ ,  $\text{H}_{8'}$ , 6.87 (dd, J 2 and 8 Hz).  
M.S.  $m/z(\%)$  333(11); 332(41); 331(7); 167(9); 166(100); 140(19); 139(15); 138(5); 115(4); 83(5); 76(3); 65(3); 63(5).

(Received in USA 7 May 1984)