Tetrahedron Letters No. 13, pp 1079 - 1082, 1975. Pergamon Press. Printed in Great Britain.

PHOTOLYSIS OF 2,2'-DIAZIDOBIPHENYL

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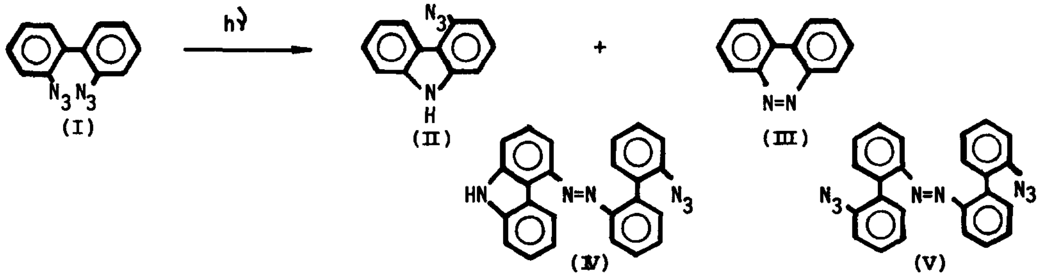
(Received in Japan 28 January 1975; received in UK for publication 18 February 1975)

Initial photochemical study on 2,2'-diazidobiphenyl (I) indicated that photolysis of (I) gave neither 4-azidocarbazole (II) nor benzo[c]cinnoline (III).[1] Recent work by J.H.Boyer and G.J.Mikol has established the formation of (II) in 50% yield and trace amounts of (III).[2] Studies on the sensitized photolysis and the photochemical mechanism of (I) have not been accomplished. In connection with the photolysis of 2-azidobiphenyl, where the direct photolysis resulted in predominant formation of carbazole and the triplet sensitization predominates the azo compound formation,[3,4] we can expect that a triplet sensitizer will increase the yield of (III) in the photolysis of (I). Another interest is photochemistry of (I) at low-temperature. In mechanistic studies on photolysis of aromatic azides, experiments at low-temperature have yielded many interesting results. However, low-temperature photochemical study on aromatic vicinal diazido compound such as (I) has not been reported. We have investigated that the direct and sensitized photolysis of (I) at room temperature, and the photolysis in glassy matrices at low-temperatures.



In the direct photolysis of (I) in n-hexane, chromatography of the photolysis product afforded three crystalline fractions. The second fraction was identified as (III) by comparison with an authentic sample. The first fraction was identified as (II) on the basis of the elementary analysis and the following spectral data[5] : (m.p. 118-120° decomp.), UVλ_{max}(ether) 343(4020),328(3500),301 (7300),292(7300),252(23000)nm ; ir(KBr) 3480(NH),2170(N_3)cm^{-1} ; ms m/e 208(M^+), 180($M^+ - N_2$) . Since (II) having one more unreacted azido group is decomposed with further irradiation, the yield of (II) decreases with increasing irradiation time after the maximum yield. The third fraction was elucidated as the coupled compound (IV) of (I) and (II) on the basis of the elementary analysis and the following spectral data : UVλ_{max}(ether) 435(9900),306(9700),250(35300)nm ; ir (KBr) 3480(NH),2170(N_3)cm^{-1} ; ms m/e 388(M^+),360($M^+ - N_2$) . Also (V) has still an azido group and is decomposed by further irradiation. Hence the yield of compounds (II) and (IV) are subject to indifinite, and chromatographically nonmobile material increases with the increase of irradiation time.

In the triplet sensitized photolysis by acetophenone or benzophenone, the main product was not the expected (III) but the intermolecular azo compound (IV), though the yield of (III) was higher than that of the direct irradiation. (V) was isolated as yellow crystals and its structural assignment was based on the following spectral data : UVλ_{max}(ether) 460(250),325(8200)nm ; ir(KBr) 2180 and 2160(N_3)cm^{-1} ; ms m/e 416(M^+),388($M^+ - N_2$),360($M^+ - 2N_2$). Though (II) was not detected within the limits of our analytical method, (IV) was formed in considerable amounts.

The photolysis of (I) in glassy matrices at low-temperature showed interesting specifity compared with that in fluid media at room temperature. The direct irradiation of 6×10^{-4}M (I) in an EPA or 3-methylpentane matrix at 77°K led to the quantitative formation of (III) directly without being trapped as nitrene (or dinitrene) intermediate. Though the formation of (II) was completely excluded at 77°K, in a glycerin matrix at 201°K (II) was formed in about 10% yield and chromatographically nonmobile material was yielded in considerable amounts.

From these results, the mechanism for the formation of carbazole (II) and

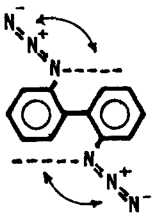
Table : Irradiations of 2,2'-Diazidobiphenyl

Run	Reactants	Solvent	Temperature	Main Product	Other Products
1	4×10^{-4}M(I)	n-Hexane	Room Temp.	(II) (65%)	(III),(IV) (trace)
2	10^{-2}M(I)	n-Hexane	Room Temp.	(II) (55%)	(III),(IV) (trace)
3	10^{-2}M(I),1.8M Acetophenone	Benzene	Room Temp.	(V) (45%)	(III),(IV) (trace)
4	10^{-2}M(I),0.5M Benzophenone	Benzene	Room Temp.	(V) (40%)	(III),(IV) (trace)
5	6×10^{-4}M(I)	EPA(5:5:2)	77°K	(III)(>98%)	
6	6×10^{-4}M(I)	3MP	77°K	(III)(>98%)	
7	5×10^{-4}M(I)	Glycerin	201°K	(III)(55%)	(II) (about 10%)

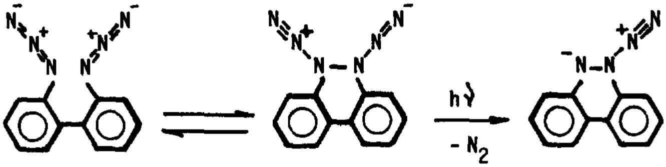
* The irradiations for the runs 1 and 2 were done using an Ushio-6DQ 6W low-pressure mercury lamp under nitrogen. For the runs 3 and 4, using an Ushio-UM-102 100W high-pressure mercury lamp under nitrogen through the filter solution of 0.13 wt.% naphthalene in ethanol. For the runs from 5 to 7, using the low-pressure lamp in a quartz cell immersed in a quartz Dewar flask filled with liquid nitrogen or solid carbon dioxide/ethanol. The yields were determined with preparative tlc and high-speed liquid chromatography followed by UV analysis.

azo compounds (III) and (V) at room temperature must be similar to that of 2-azidobiphenyl. The direct irradiation of (I) leads exclusively to the formation of (II) , and the azo compound formation is almost negligible. In the triplet sensitized photolysis, the predominant formation of intermolecular azo compound (V) instead of the expected intramolecular one (III) could be explained in the terms of a rather long-lived intermediate (nitrene) and structural factor of o,o'-disubstituted biphenyl. 2-Azido-2'-nitrenobiphenyl, which is estimated to be intermediate in the azo compound (V) formation, has presumably enough longer life-time, compared with diffusion rate, to react bimolecularly. On the other hand, the azido groups is partly free to rotate about the C-N bond at room temperature and they must be situated in positions which are far apart each other such as (Ia). These factors support the intermolecular azo compound formation rather than intramolecular one.

The photolysis of (I) in rigid matrices at low-temperature is a specific process different from not only that at room temperature but that of 2-azidobiphenyl. It has been reported that the irradiation of 2-azidobiphenyl in



(Ia)



(Ib) (Ic) (Id)

rigid matrices at 77°K led firstly to 2-nitrenobiphenyl and further irradiation yielded carbazole quantitatively.[6] Why, in the case of (I), does the specific intramolecular azo-bond formation proceed exclusively, and why is the carbazole formation excluded ? First it is clear that matrix rigidity hinders the easier bimolecular reaction in fluid media. Hence the intermolecular azo-bond formation would be suppressed. Secondly we must consider azide-azide intramolecular interaction. Though the configuration of (I) is estimated such as (Ia), at 77°K the rotation about the C-N bond is locked in the plane of the ring.[7] When the azido groups is locked in a state of non-hinderance, the activation energy for the rotation of the benzene rings must be lowered to only a few Kcal/mol. On the other hand, an activation energy for the carbazole formation in 2-nitrenobiphenyl has been estimated to be about 8 or 11.46 Kcal/mol.[4,7] These data support the specific intramolecular azo-bond formation. Therefore, it may be considered for the low-temperature photolysis to proceed through such structures as (Ib) and (Ic), which are favorable to form (III). Details of the discussion on mechanism and further studies will be published in the near future.

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