228. On the Mechanism of the Thermal and Photolytic Cyclization of Diphenylamines to Carbazoles

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Summary. The product of photolysis of di-*p*-tolylamine in petroleum ether is 3,6-dimethylcarbazole. The primary product of gas-phase thermolysis of di-*p*-tolylamine at 850–1000°/0.01–0.05 Torr is also 3,6-dimethylcarbazole. In the higher temperature range monomethylcarbazole and carbazole are also formed. Thermolysis of tetra-*p*-tolylhydrazine at 800–1000° gives only di-*p*-tolylamine, the latter decomposing further in the higher temperature range. It is concluded that carbazole formation involves in both cases an electrocyclization of the *ortho*-positions, and not a rearrangement, and that diphenylaminyl is not an intermediate.

It was reported [1] already in 1896 that thermolysis of *o*-toluidine gave a dimethylcarbazole, m.p. 183–184°, possibly [2] the 1,8-dimethyl-isomer. 1,8-Dimethylcarbazole is, however, recorded [3] to have a m.p. of 175–176°. Much later it was published [4], without any evidence or reference, that di-*o*-tolylamine on photolysis in petroleum ether gave 1,8-dimethylcarbazole, m.p. 49–50°. We felt that the recorded m.p. discrepancies and lack of reliable identification warranted a reinvestigation, and therefore we have examined the photolysis and thermolysis of di-*p*-tolylamine (**1**).

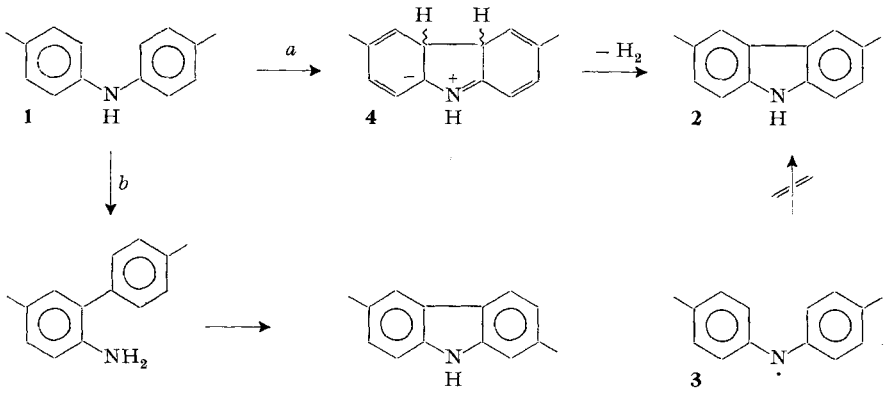
Photolysis of **1** in petroleum ether and isolation of the product by column chromatography gave 3,6-dimethylcarbazole (**2**), identified by its m.p. and picrate, as well as by IR., NMR., and mass spectrometry. The NMR. spectrum, interpreted by comparison with the known spectrum of carbazole [5], is in complete accord with the substituent pattern of **2**. The broad low-field peak at δ 7,85 is due to H-C4 which is long-range coupled to N–H [5]. H-C1 and H-C2 give rise to two doublets, the high-field H-C2 being coupled further to H-C4.

Gas-phase thermolysis of diphenylamine gave carbazole [6] and fragmentation products (see Experimental). In the thermolyses of di-*p*-tolylamine the degree of conversion was kept low in order to suppress fragmentation. Thermolysis of **1** commenced at 800°C/0.01 Torr. The carbazole fraction isolated after thermolysis at 850° was found by gas chromatography and mass spectrometry to consist of 90% dimethylcarbazole, 9% methylcarbazole (not further examined), and 1% carbazole. Demethylation increased with the temperature: at 1000° 80% pure carbazole was isolated. The dimethylcarbazole formed at 850° and 900° was identified as **2** by spectral comparison with the product of photolysis.

The possible intermediacy of di-*p*-tolylaminyl (**3**) was excluded by thermolysis of tetra-*p*-tolylhydrazine which is known [7] to dissociate to **3** under mild conditions. At 800°/0.01 Torr the sole collected product was di-*p*-tolylamine (**1**), arising from hydrogen capture by the aminyl **3**. At 800–1000° **1** was still the main product, accompanied by a low yield of the thermolysis products of **1**.

The results are in accord with the electrocyclic reaction pathway (*a* in the Scheme) both for photolysis and thermolysis. Such a mechanism has been previously assumed

for the photolytic reaction [4] [8]. Any mechanism involving aminyl formation or rearrangement, *e.g.* analogous with the one reported [9] to occur in diphenylamine by electrical discharge (path *b* in the Scheme), is discredited.



The carbazole formation is therefore analogous with the well-known photolytic [10] and thermal [11] cyclization of the isoelectronic *cis*-stilbene to phenanthrene. Orbital symmetry considerations [12] indicate that the only difference (apart from electronic states) between the thermal and the photolytic reactions should be that the former gives a *cis*-dihydro intermediate, **4**, the latter a *trans*-dihydro intermediate (*cf.* [8] [10] [13]). Our results also allow an easy explanation of the formation of carbazole in the gas-phase thermolysis of phenyl azide, which has been postulated to involve a novel addition of phenylnitrene to benzene [14]. Aniline and azobenzene are primary thermolysis products of phenylnitrene; both react further to diphenylamine [6] [15], which, as shown above, is a source of carbazole in the temperature range where phenyl azide gives the same product:

$$Ph{-}N_3 \xrightarrow{\Delta} Ph{-}\ddot{N}{:} \rightarrow Ph{-}NH_2 + Ph{-}N{=}N{-}Ph \rightarrow Ph{-}NH{-}Ph \rightarrow \text{carbazole}$$

Experimental. – 1. *General.* The pyrolysis apparatus consisted of a 30 × 2 cm quartz tube, empty or packed with small pieces of quartz tubing, heated by a *Heraeus* oven, type Rok 3/30, with automatic temperature control, type AR 101. The apparatus was held at an ultimate vacuum of 10^{-3} Torr (measured on a *Vacustat* near the pump). Products were collected in a trap cooled in liq. N_2. Gas chromatography was on a *Carlo Erba* FRACTOVAP model G1. NMR. spectra were recorded on a *Varian* A-60 A instrument coupled to a C-1024 time averaging computer. Mass spectra were recorded on a CEC 21-490 instrument with source temperature 200° and direct inlet. M.p.'s are uncorrected.

2. *Photolysis of di-p-tolylamine.* A 0.005 M solution of **1** in petroleum ether (b.p. 30–60°) was irradiated for 40 h at room temperature with a 450 W Hg-lamp (*cf.* [4] [13]). After fractional recrystallisation from petroleum ether or column chromatography (alumina/benzene-petroleum ether 30:70) and sublimation, the product was identified as 3,6-dimethylcarbazole (**2**): m.p. 219–220° (lit. [3]: 217–218°; [16]: 219°), picrate (from benzene) m.p. 191–192° (lit. [3] [16]: 192°), IR. (in KBr): NH at 3400 cm^{-1}, NMR. (in acetone-d_6): δ 2.55 (CH_3, *s*), 7.26 (H-C2, *q*, $J_{1,2}$ 8.2 Hz, $J_{2,4}$ = 1.5 Hz), 7.43 (H-Cl, *d*, $J_{1,2}$ = 8.2 Hz), 7.85 (H-C4, *s*, broadened by $J_{1,4}$ and $J_{4,9}$); mass spectrum (70 eV), ions (rel. int.): M^+ = 195 (100), $M-1$ (56), $M-CH_3$ (13), $M-2CH_3$ (3.5), $[M-2H]^{2+}$ (45), $[M-2H-26]^{2+}$ (18) (formed from $[M-2H]^{2+}$, m^* 72.2).

3. *Pyrolysis of diphenylamine.* 1.0 g of diphenylamine was distilled at 110° during 1 h into the packed tube heated at 1000°/0.05 Torr. The pyrolysate was extracted with acetone, the extract

filtered through active carbon and evaporated to give 0.93 g yellow crystalline material. Gas chromatography (1,5 m × 5 mm column of 5% Carbowax 20M on Aeropak, He carrier 60 ml/min, injector 300°, column 200°) of a benzene solution of this material gave as major products: benzonitrile (10%), aniline (17%), biphenyl (2%), carbazole (35%), and recovered diphenylamine (20%).

4. *Pyrolysis of di-*p*-tolylamine.* 1–5 g **1** was distilled at 105–115° during 5–8 h into the packed tube heated between 800 and 1000°/0.01–0.05 Torr. The pyrolysate was chromatographed on alumina. The product eluted with benzene-petroleum ether (30:70) was purified by fractional recrystallisation from petroleum ether and/or preparative thin-layer chromatography (silica gel GF_{254}/benzene-petroleum ether 30:70) followed by sublimation (see Table). Individual carbazoles in mixture were assayed by mass spectrometry at 7.5 eV and gas chromatography (1.5 m × 5 mm column of 2% polyethylene glycol 20000 on cellite 545 (80–100 mesh), N_2 carrier 3 kg/cm², injector 300°, column 260°). The 3,6-dimethylcarbazole formed at 850° and 900° was identified by comparison of the NMR. spectrum with that of the photolysis product (*vide supra*, 2).

*Carbazole products of pyrolysis of di-*p*-tolylamine*

Pyrolysis temperature °C	Pyrolysis yield %	Relative yields		
		Carbazole	Methyl-carbazole	3,6-Dimethyl-carbazole
850	0.25	1	9	90
900	2.5	4	17	79
1000	0.3	80	20	0.6

5. *Pyrolysis of tetra-*p*-tolylhydrazine:* 500 mg was sublimed at 70–80° into the empty pyrolysis tube, maintained at 800°. The collected product was found by thin layer chromatography to contain starting material and **1**, but no carbazoles. The product from pyrolysis at 1000° showed a large spot due to **1**, and minor spots corresponding to the products of pyrolysis of **1** at 1000°.

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BIBLIOGRAPHY

[1] *H. Seyberth*, Ber. deutsch. chem. Ges. *29*, 2594 (1896).
[2] Beilsteins Handb. org. Chem. *XX*, 448.
[3] *I. C. S. Barnes, K. H. Pausacker & C. I. Schubert*, J. chem. Soc. *1949*, 1381.
[4] *W. Carruthers*, Chem. Commun. *1966*, 272.
[5] *P. J. Black & M. L. Heffernan*, Aust. J. Chem. *18*, 353 (1965).
[6] Cf. *C. Graebe*, Ber. deutsch. chem. Ges. *5*, 376 (1872); Liebigs Ann. Chem. *167*, 125 (1873); *174*, 177 (1874).
[7] *H. Wieland & H. Lecher*, Liebigs Ann. Chem. *392*, 156 (1912); *H. Wieland, ibid. 381*, 200 (1911); *F. A. Neugebauer & P. H. H. Fischer*, Chem. Ber. *98*, 844 (1965); *F. A. Neugebauer & S. Bamberger*, Angew. Chem. *83*, 47 (1971).
[8] *H. Linschitz & K.-H. Grellmann*, J. amer. chem. Soc. *86*, 304 (1964); *K.-H. Grellmann, G. M. Sherman & H. Linschitz, ibid. 85*, 1881 (1963); *T. Hinohara*, Nippon Kagaku Zasshi *90*, 860 (1969); *H. Shizuka, Y. Takayama, I. Tanaka & T. Morita*, J. amer. chem. Soc. *92*, 7270 (1970).
[9] *H. Suhr, U. Schöch & G. Rosskamp*, Chem. Ber. *104*, 674 (1971).
[10] *F. R. Mallory, C. S. Wood & J. T. Gordon*, J. amer. chem. Soc. *86*, 3094 (1964).
[11] *T. C. Jones & I. Schmeltz*, J. org. Chemistry *34*, 645 (1969).
[12] *R. B. Woodward & R. Hoffmann*, Angew. Chem. *81*, 797 (1969); *K. A. Muszkat & W. Schmidt*, Helv. *54*, 1195 (1971).

[13] *E. J. Bowen & J. H. D. Eland*, Proc. chem. Soc. *1963*, 202.
[14] *E. Hedaya, M. E. Kent, D. W. McNeil, F. P. Lossing & T. McAllister*, Tetrahedron Letters *1968*, 3415.
[15] *C. Wentrup*, Ph. D. Thesis, Australian National University, Canberra 1969.
[16] *E. Täuber & R. Loewenherz*, Ber. deutsch. chem. Ges. *24*, 1033 (1891).

229. Photoinduzierte nucleophile Substitution von 3-substituierten 2,1-Benzisoxazolen (unter Ringöffnung)

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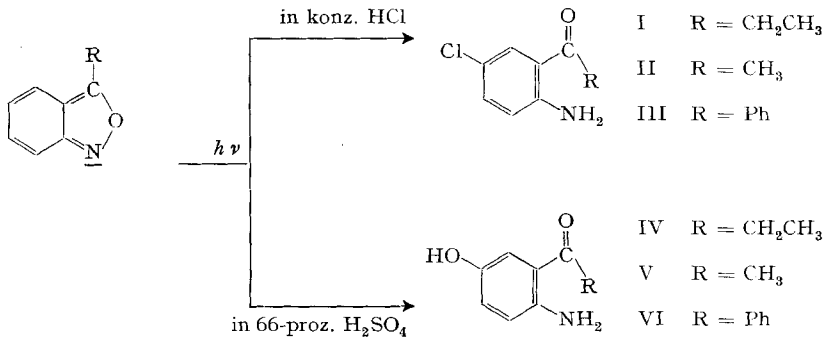
Summary. On UV.-irradiation in strongly acidic solution 3-alkyl- and 3-aryl-2,1 benzisoxazoles, respectively, yield 5-substituted 2-aminophenylketons.

UV.-Bestrahlung von 3-Alkyl- und 3-Aryl-2,1-benzisoxazolen (Alkyl- bzw. Arylanthranilen) in konz. saurer Lösung bewirkt Öffnung des Heteroringes und Substitution des Benzolringes: das Anion der verwendeten Säure tritt in *p*-Stellung zum N-Atom des Benzisoxazols; bei Verwendung von Schwefelsäure wird der primär entstandene Schwefelsäureester unter Bildung einer Hydroxyverbindung hydrolysiert.



Man kann als einleitenden Schritt eine photoinduzierte Homolyse (a) der O–N-σ-Bindung annehmen. Da aber das N-Atom protoniert ist, kann auch eine Heterolyse (b) derselben Bindung in der durch die Bestrahlung angeregten Molekel in Betracht gezogen werden. Das entstandene Kation *K* (in der Grenzform rechts) wird hierauf vom in der Lösung anwesenden Anion der Säure in *p*-Stellung nucleophil angegriffen, worauf – wahrscheinlich auf dem aufgezeichneten Wege – die entsprechenden substituierten 2-Aminophenylketone entstehen (S. 2112). Im Falle $A^- = HSO_4^-$ erhält man, wie schon erwähnt, die entsprechenden Hydroxy- derivate IV, V und VI.

Diese photoinduzierte Reaktion dürfte sonst schwer erhaltbare, in 5-Stellung substituierte 2-Aminophenylketone leicht zugänglich machen.

[1]) Zum Teil aus der Dissertation von *Jorge Rosales*, Univ. Fribourg 1963.