BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 2066—2068 (1969)

The Rearrangement of 2-Aminobenzophenones

Kakuzo Isagawa, Takumi Ishiwaka, (the late) Masamichi Kawai
and Yasaburo Fushizaki

Department of Applied Chemistry, Faculty of Engineering, University of Osaka Prefecture, Sakai, Osaka

(Received November 6, 1968)

A previous paper[1] described how 2-amino-5-chlorobenzophenone (Ib) afforded the intermolecular condensation product, 2,8-dichloro-6,12-diphenyldibenzo[*b*,*f*]-1,5-diazocine (IIb), under the several sets of conditions.[2]

This report will deal with the rearrangement of aminobenzophenones (I) to benzanilides (III) by treating them with zinc chloride.

It has been reported that the migration of acetyl, propionyl, and benzoyl groups occurred when the *N*-monoacyl- or *N*,*N*-diacylaniline was heated for a long time with anhydrous aluminum chloride or zinc chloride, and that the migration groups entered into the *o*-position or, preferably, the *p*-position.[3–5] On the other hand, 9-acridone was prepared from 2-aminobenzophenone in the presence of lead

---

[1] M. Kawai, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **88**, 102 (1967).

[2] W. Metlesics, T. Reanick, G. Silverman, R. Tavares and L. H. Sternbach, *J. Med. Chem.*, **9**, 633 (1966).

[3] J. F. J. Dippy and J. H. Wood, *J. Chem. Soc.*, **1949**, 2719.

[4] J. F. J. Dippy and V. Moss, *ibid.*, **1952**, 2205.

[5] F. D. Chattaway, *ibid.*, **1904**, 386.

monoxide,[6] and a series of 2-amino-2′-fluorobenzophenones, upon treatment with potassium carbonate in *N*,*N*-dimethylformamide, underwent internal nucleophilic exchange to give the corresponding 9-acridones.[7]

We have now found that the treatment of I with zinc chloride gave benzanilides (III) and 9-acridones (IV), together with dibenzodiazocines (II). In this reaction, the rearrangement of I to III was brought about, and the benzoyl group migrated from the carbon of the aromatic nucleus to the nitrogen of the amino group. At the same time, I underwent dehydrocyclization to IV.

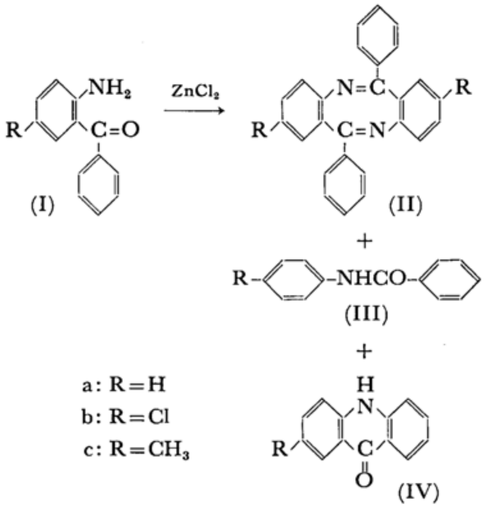

TABLE 1. TREATMENT OF 2-AMINOBENZOPHENONES WITH $ZnCl_2$ OR $AlCl_3$

Attempted compound	Catalyst	Temp. °C	Products, %[a)] Diazocine	Anilide	Acridone
Ia	$ZnCl_2$	200	22.0	4.1	trace
Ia	$ZnCl_2$	220	21.5	3.8	trace
Ib	$ZnCl_2$	180	67.9	trace	—
Ib	$ZnCl_2$	200	43.3	7.9	trace
Ib	$ZnCl_3$	220	10.1	14.3	trace
Ib	$ZnCl_2$	240	8.2	4.8	trace
Ib	—	200	41.7	—	—
Ib	$AlCl_3$	200	77.5	trace	—
Ic	$ZnCl_2$	200	17.9	1.7	trace
Ic	$ZnCl_2$	220	11.4	trace	trace

a) Theoretical yield, based on aminobenzophenones.

Table 1 presents the results obtained under suitable conditions.

As may be seen in Table 1, Ib scarcely rearranged to IIIb at all in the presence of aluminum chloride. However, the rearrangement proceeded well when zinc chloride was used as the catalyst. When the mixture was heated at 200°C or 220°C, the yields of anilides increased in the following order: $R=CH_3<H<Cl$, where R is as shown in the synthetic scheme. As for the reverse reaction, Dippy and Moss reported that the percentage conversion into 2-aminobenzophenones was 15% for IIIb and 5% for IIIc.[4] Furthermore, these authors described how a monoacyl and a *N*,*N*-diacylaniline rearranged by an intermolecular mechanism, since the acyl group could be removed in the form of acyl chloride. In our experiment, a small amount of benzoic acid was produced upon the treatment of Ia with zinc chloride.

Experimental

Treatment of 2-Aminobenzophenones with $ZnCl_2$ or $AlCl_3$. Only a typical reaction will be described here. All of these reactions were carried out by a method similar to that described below.

To 4.63 g (0.02 mol) of Ib heated to 120°C there were added 2.6 g of zinc chloride. The mixture was then heated to the temperature shown in Table 1 for ten hours. After cooling to room temperature, 100 m*l* of warm water and 200 m*l* of chloroform were added to the reaction mixture; brownish, insoluble solids were filtered off. The aqueous layer was separated and discarded. The organic layer was dried over anhydrous potassium carbonate, filtered, and concentraed to dryness *in vacuo*. The residue was dissolved in a mixture of chloroform and carbon tetrachloride (1 : 1) and chromatographed on a column of silica gel. The residue remaining after the evaporation of the first eluate was added to 20 m*l* of methanol. The insoluble material, diazocine IIb, was recrystallized from a mixture of methanol and methylene chloride to give yellow prisms; mp 219—220°C (lit[1,2] mp 219—220°C). IR:*[1] 1615, 890, 854 cm^{-1}. (Found: C, 72.92; H, 3.60; N, 6.34; Cl, 16.59%).

The mother liquors were concentrated to dryness *in vacuo*, and the residue was added to carbon tetrachloride and filtered. The insoluble material, 4′-chlorobenzanilide IIIb, was recrystallized from methylene chloride to give colorless needles; mp 190—192°C (lit[8] mp 192—193°C). IR: 3300, 1650 cm^{-1}. NMR:*[2] δ 10.06 (broad singlet, 1H, NH), δ 8.06—7.27 (multiplet, 9H, aromatic protons). (Found: C, 67.59; H, 4.40; N, 6.33%).

2-Chloro-9-acridone (IVb) was afforded from an eluate of the second band (blue-violet fluorescence). The second eluate was concentrated to dryness *in vacuo*, and the residue was recrystallized from *N*,*N*-dimethylformamide to give bright yellow prisms; mp>320°C (lit[9] mp>360°C). IR: 1635, 1600, 1560 cm^{-1}. (Found: C, 67.78; H, 3.49; N, 6.23%).

Identification of the Other Products. The diazocines, anilides, and acridones were identified by

---

[6] C. Graebe and F. Ullmann, *Ber.*, **27**, 3483 (1894).

[7] R. I. Fryer, J. Early and L. H. Sternbach, *J. Chem. Soc.*, **1963**, 4979.

*[1] Taken on KBr tablets.

*[2] Measured in $CDCl_3$ - DMSO (4 : 1); tetramethylsilane as the internal standard.

[8] R. von Walther, *J. prakt. Chem.*, [2], **58**, 160 (1903).

[9] F. Ullmann, *Ann.*, **355**, 339 (1907).

means of mixed-melting-point measurements, and by a comparison of these IR and/or NMR spectra with those of authentic samples synthesized by the methods cited below or by similar methods.

6,12-Diphenyldibenzo[b,f]-1,5-diazocine (*IIa*).[1,2] Mp: 190—192°C. IR: 1620, 770 cm^{-1}.

2,8-Dimethyl-6,12-diphenyldibenzo [b,f]-1,5-diazocine (*IIc*).[1] Mp: 195—196°C. IR: 1620, 870, 820 cm^{-1}.

Benzanilide (*IIIa*).[10] Mp: 162—163°C. IR: 3300, 1650 cm^{-1}. NMR: δ 9.82 (broad singlet, 1H, NH), δ 8.09—7.10 (multiplet, 10H, aromatic protons).

4'-Methylbenzanilide (*IIIc*).[10] Mp: 156—158°C. IR: 3320, 1650 cm^{-1}. NMR: δ 9.62 (broad singlet, 1H, NH), δ 8.05—7.08 (multiplet, 9H, aromatic protons), δ 2.32 (singlet, 3H, CH_3).

9-*Acridone* (*IVa*).[11] Mp: >320°C. IR: 1635, 1600, 1560 cm^{-1}.

2-*Methyl-9-acridone* (*IVc*).[11] Mp: >320°C. IR: 1635, 1600, 1560 cm^{-1}.

---

[10] C. N. Webb, "Organic Syntheses," Coll. Vol. I, p. 82 (1941).

[11] C. F. H. Allen and G. H. W. McKee, *ibid.*, Coll. Vol. II, p. 15 (1943).