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The Beckmann Rearrangement of *p*-Nitrobenzophenone Oxime with Thionyl Chloride

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As is well known, many works on the Beckmann rearrangement have been reported.[1] Generally, it has been shown that the rearrangement is brought about by acids including Lewis acids, and that the mechanism proceeds in the migration of the *trans*-substituent for the hydroxyl group into the nitrogen atom (*trans*-migration).

Recently, Yukawa has reported the migratory aptitude in the Beckmann rearrangement varies according to the kind of catalysts.[2] However, the details have not yet been published. The authors are interested in this point and have done the present work seeking a clue to elucidate the effect of a migrating catalyst on the Beckmann rearrangement.

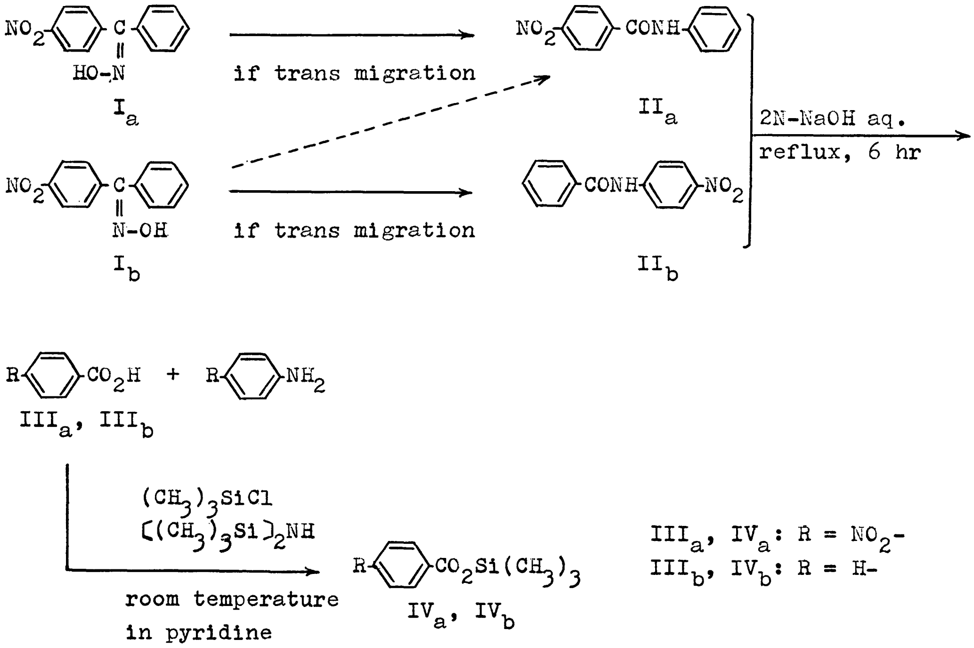
p-Nitrobenzophenone oxime I was chosen as the starting material, because it can be purified and separated into *syn*- and *anti*-isomers readily. The Beckmann rearrangements of this oxime with phosphorus pentachloride[3] and phosphoryl chloride[4] have been reported in the migration of the *trans*-substituent for the hydroxyl group. For the present paper, the authors chose thionyl chloride as the migrating catalyst, and the reactions were carried out in both benzene and chloroform.

Results and Discussion

p-Nitrobenzophenone oxime I was separated into *syn*- and *anti*-isomers (Ia and Ib) by the method of Sutton.[3] To the solution of Ia or Ib we then slowly stirred three equivalent moles of thionyl chloride. The given amides II were hydrolysed with an aqueous sodium hydroxide solution, and then aromatic acids were separated. These aromatic acids, IIIa and IIIb, were silylated with trimethylchlorosilane and hexamethyldisilazane to form volatile derivatives. That procedure is shown in Scheme 1. These silyl esters, IVa and IVb were determined quantitatively by gas-liquid chromatography, using methyl *p*-nitrobenzoate as the internal standard substance.[5]

The results are shown in Table 1. On the basis of these results, the following conclusions are deduced.

1) On using thionyl chloride as a migrating catalyst, only phenyl group which is situated in the *trans* position for the hydroxyl group in Ia migrated (*trans* migration), while in Ib either a *trans* or a *cis* migration took place simultaneously. It appears that Ib isomerized into Ia, along with a small amount of hydrogen chloride which



Scheme 1

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[1] a) A. H. Blatt, *Chem. Rev.*, **12**, 215 (1933); b) E. C. Franklin, *ibid.*, **14**, 219 (1934); c) B. Jones, *ibid.*, **35** 335 (1944); d) M. Kotake, "Jikken Kagaku, Koza," Vol. 18, Maruzen Co., Tokyo (1957), p. 417; e) M. Murakami, "Yukihannokikō no Shinpo," Vol. 1, Maki Shoten, Tokyo (1958), p. 189; f) L. G. Donaruma and W. Z. Heldt, "Organic Reactions," Vol. 11, John Wiley & Sons, New York and London (1960), p. 1.

[2] See 1) d) Y. Yukawa, p. 426.

[3] L. Brady and R. P. Mehta, *J. Chem. Soc.*, **125**, 2297 (1924); L. E. Sutton and T. W. J. Taylor, *ibid.*, **1931**, 2190.

[4] J. Meisenheimer and G. Gaiser, *Ann. Chem.*, **539**. 95 (1939).

[5] Z. Horii, M. Makita, I. Takeda, Y. Tamura, and Y. Ohnishi, *Chem. Pharm. Bull.* (Tokyo), **13**, 636 (1965).

TABLE 1. MIGRATORY APTITUDE OF *p*-NITROBENZOPHENONE OXIME

Oxime	Migrating catalyst	Solvent	Reaction temperature °C	Ratio of TMS ester of acid IVa:IVb	Migratory aptitude
Ia	$SOCl_2$	Benzene	10	only IVa[a]	*trans*
			26	only IVa[a]	*trans*
		Chloroform	10	only IVa[a]	*trans*
			26	only IVa[a]	*trans*
	PCl_5	Benzene	29	only IVa[a]	*trans*
Ib	$SOCl_2$	Benzene	10	82:18	*cis* : *trans*
			26	80:20	*cis* : *trans*
			20	81:19	*cis* : *trans*
		Chloroform	−8	50:50	*cis* : *trans*
			26	69:31	*cis* : *trans*
			58	45:55	*cis* : *trans*
	PCl_5	Benzene	29	only IVb	*trans*

a) The given amide was identical with authentic sample which was prepared from aniline and *p*-nitrobenzoic acid.

was produced in the reaction system; then Ia was rearranged into IIa with thionyl chloride.[6] At any rate, it is necessary to measure both the isomerizing and migrating rates of Ib in order to clarify the mechanism in detail.

2) The *cis* migrating ratio in benzene predominates over that in chloroform. It appears that the migration proceeds faster than the isomerization in chloroform, because generally the migrating rate in the Beckmann rearrangement increases in a polar solvent.[7]

3) Within the limits of these experiments, the migrating aptitudes are independent of the reaction temperature.

4) Regardless of whether the oxime is of the *syn-* or *anti*-form, only the *trans* migration took place with phosphorus pentachloride.

It is clear from the above conclusions that the migratory aptitude varies greatly with the migrating catalyst and that it is affected by the stability of "*anti*-oxime" for a catalyst.

Experimental

p-*Nitrobenzophenone*. *p*-Nitrobenzophenone was prepared by the method of Schroether.[8] Mp 138°C (recrystallized from acetic acid); yield, 80%.

syn- *and* anti-p-*Nitrobenzophenone oxime Ia, Ib.* *p*-Nitrobenzophenone oxime I was prepared by the method of Brady.[3] Mp 108—116°C. *syn-* and *anti*-Oximes were separated by the method of Sutton.[3] Ia: mp 158°C; yield, 25%; NMR spectrum, 11.69 ppm in DMSO (*syn*-=N-OH). Ib: mp 136°C; yield, 25%; NMR spectrum, 11.88 ppm in DMSO (*anti*-=N-OH). The IR spectrum of Ia was identical with that of Ib.

Purification of Thionyl Chloride. Commercial-grade thionyl chloride was further purified by the method of Fieser.[9] Bp 76°C; colorless.

The Beckmann Rearrangement of p-*Nitrobenzophenone Oxime.* Into 1.2 g (0.005 mol) of oxime in anhydrous benzene (5 m*l*) we stirred thionyl chloride (1.1 m*l*, 0.015 mol) in benzene (2.5 m*l*). The reaction was carried out for 30 min at the temperatures shown in Table 1. After the solution has then been left standing for a night, the excess amount of thionyl chloride was decomposed with water, and the benzene was removed. The precipitate was filtered and used for the following procedure. In each case, the product was obtained quantitatively.

Hydrolysis of the Given Amide. To a given amide (0.6 g) we added a 2N sodium hydroxide aqueous solution (13 m*l*), after which the mixture was refluxed in an oil bath at 140°C for 6 hr. The solution was then cooled to room temperature and neutralized with hydrochloric acid. The precipitate was filtered and dried in a desiccator. The aromatic acid was obtained quantitatively.

Silylation and Quantitative Determination of Aromatic Acids. III. The aromatic acids were convertedi nto their volatile trimethylsilyl derivatives and were determined quantitatively by a modification of the method of Horii.[5] To crude III (0.04 g) in dry pyridine (0.6 m*l*), we added trimethylchlorosilane (0.2 m*l*) and then hexamethyldisilazane (0.2 m*l*). The formation of their trimethylsilyl derivatives occurred very rapidly at room temperature; after the pyridine hydrochloride has been removed by means of centrifuge, within a few minutes the entire reaction mixture was injected directly into the chromatograph.

Instrument: Yanagimoto GCG–550T.
Conditions: Column, 2 m×3 mmϕ
Column packing, 40% Silicone DC–Hv grease on 60-80 mesh Celite 545.
Column temperature, 170°C (Determination for IVa) 150°C (Determination for IVb)
H_2 flow rate, 40 m*l* per min.

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[6] The oxime Ib was isomerized into Ia with hydrogen chloride at room temperature, but Ib did not rearrange into amide under the same conditions.

[7] J. Meisenheimer, *Ber.*, **54**, 3206 (1921); A. W. Chapman *et al.*, *J. Chem. Soc.*, **1933**, 806; **1934**, 1550; **1935**, 1223.

[8] G. Schroether, *Ber.*, **42**, 3360 (1909).

[9] L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed., D. C Heath and Co., Boston (1955), p. 345.