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THE AROMATIZATION OF CYCLOHEXANEDIONE DIOXIMES

Y. KOBAYASHI and S. WAKAMATSU
Nagoya Research Laboratory, Toyo Rayon Co., Minatoku, Nagoya, Japan

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Abstract—The aromatization of cyclohexane-1,2-dione dioxime (nioxime), 4-methylcyclohexane-1,2-dione dioxime and nickel (II)bis(N,N'-4-methylcyclohexane-1,2-dione dioximate) takes place in polyphosphoric acid (PPA) to the corresponding *o*-phenylenediamine derivatives. The mechanism is analogous to the Semmler-Wolff aromatization.

Aromatization, in addition to the normal Beckmann rearrangement, takes place with cyclohexane 1,4-dione dioxime in both conc and fuming sulfuric acids.

THE Beckmann rearrangement of cyclohexane-1,2-dione dioxime (nioxime; I) depends on the catalytic reagents used—cyclohexano-[c]-1,2,5-oxadiazole,[1] 1-aza-7-oximinocyclohepta-2-one[2] and δ-cyanovaleric acid,[2] being produced by direct dehydrative condensation, the Beckmann rearrangement of one of two oximino groups and a ring cleavage reaction, respectively.

The formation of the first product from I represents a typical Beckmann rearrangement of *vic*-dioximes,[3] which usually do not yield corresponding amides, but dehydrate directly or first rearrange partially and then dehydrate to give 1,2,5-oxadiazoles or 1,2,4-oxadiazoles, respectively. Investigation of the Beckmann rearrangement of I revealed that in conc sulfuric acid I does not afford the above reported compounds, but is preferentially aromatized to *o*-phenylenediamine (21%, II), adipic acid (1·7%, III) and a small amount of an amide which is likely to be 1,8-diaza-2,7-dioxocyclooctane (IV).

The identification of IV was unsatisfactory, although it showed a strong amide band I at 1675 cm^{-1}. The examination of the hydrolysates showed that the compound is probably a lactam composed of a diamine and a dicarboxylic acid, which may be hydrazine and adipic acid, respectively. 4-Methylcyclohexane-1,2-dione dioxime (V) and its nickel chelate compound, nickel(II)bis(N,N'-4-methylcyclohexane-1,2-dione dioximate) (VI), were also aromatized by PPA to yield 3,4-diaminotoluene (VII). As 3-methylcyclohexane-1,2-dione dioxime (VIII) does not afford 2,3-diaminotoluene in either conc sulfuric acid or PPA, alkyl substitution of the carbon atom adjacent to the oximino groups in cyclohexane ring interferes with the aromatization reaction. PPA, conc and fuming sulfuric acids are good reagents for the aromatization, PPA being more effective. Although dilute sulfuric acid yields traces of the aromatic diamines, phosphoric acid, phosphorus pentachloride in ether, *p*-toluenesulfonyl chloride in aqueous sodium hydroxide and Beckmann's mixture composed of acetic

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[1] N. Tokura, R. Tada and K. Yokoyama, *Bull Chem. Soc. Japan* **34**, 270 (1961).

[2] N. Tokura, R. Tada and K. Yokoyama, *Bull. Chem. Soc. Japan* **34**, 1812 (1961).

[3] [a] See the review on Beckmann rearrangement by L. G. Donaruma and W. Z. Held, *Organic Reactions* Vol. 11, p. 37. Wiley, New York (1960); [b] R. T. Conley and F. A. Mikulski, *J. Org. Chem.* **24**, 97 (1959); [c] N. Tokura, I. Shirai and T. Sugahara, *Bull. Chem. Soc. Japan* **35**, 722 (1962).

acid and acetic acid anhydride saturated with hydrogen chloride do not afford the aromatic diamines.

The Semmler-Wolff aromatization of cyclohexenone oximes[4] and cyclohexadienone oximes[5] have been reported. In the Beckmann rearrangement of cyclohexanone oxime with sulfuric acid the formation of trace amount ($10^{-3}\%$) of aniline also has been reported.[6] This provides the possibility that the aromatization of oximes is not restricted to the oximes of unsaturated cyclohexene derivatives, as indicated by the preferential formation of aromatic diamines from cyclohexane-1,2-dione dioximes. This reaction is analogous to the Semmler-Wolff aromatization in that tautomerization of Ia and Va to Ib and Vb, respectively, leads to XIIa according to the Semmler-Wolff reaction path.[4b,e]

Compound XIIa tautomerizes to XIIb which is transformed to aromatic diamines II, VIII by the mechanism similar to that of cyclohexadienone oximes.[5] The fact that 2,3-diaminotoluene is not formed may be due to the interference with prototropy IX→Xa by the electron releasing methyl group.

The aromatization of the cyclohexane-1,2-dione dioximes is in contrast to the reaction of cyclohexenone oximes which are aromatized with Beckmann's mixture or aqueous hydrochloric acid but with PPA[7] or sulfuric acid[8] undergo normal Beckmann rearrangement.

The formation of adipic acid is facilitated by the adjacent oximino groups which stabilize the carbonium ion or the incipient positive charge formed during cleavage.

The Beckmann rearrangement of cyclohexane-1,4-dione dioxime (XIV) with *p*-toluenesulfonic acid or fuming sulfuric acid was reported by Knunyants,[9] Hall[10] and Rothe[11] to yield 1,5-diaza-4,8-dioxocyclooctane (XV) and 1,4-diaza-5,8-dioxocyclooctane (XVI). On the other hand, *p*-phenylenediamine (XVIII) and 2-chloro-*p*-phenylenediamine are produced by treatment of XIV[12] and its monohydrochloride monohydrate with PPA[13], respectively.

Re-examination of the reaction of XIV in both conc and fuming sulfuric acids confirmed that 1,5-diaza-4,8-dioxocyclooctane, ethylenediamine (XVIII), succinic acid (XIX) are formed together with *p*-phenylenediamine.

The isolation of *p*-phenylenediamine from other products was successful only with picryl chloride because of the resins formed.

This indicates simultaneous Beckmann rearrangement and Semmler-Wolff

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[4] [a] N. N. Vorozhtsov and V. A. Kopting, *J. Gen. Chem. U.S.S.R.* **28**, 1697 (1958), have summarized details of the reaction published previously; [b] M. V. Bhatt, *Experientia* **13**, 70 (1957); [c] A. R. Collicut and G. Johnes, *J. Chem. Soc.* 4101 (1960); [d] R. T. Conley, *Experientia* **15**, 497 (1962); [e] L. Banger and R. E. Hewitson, *J. Org. Chem.* **27**, 3982 (1962); [f] S. Nizamuddin and D. N. Chandlurry, *J. Indian Chem. Soc.* **40**, 960 (1963); [g] J. Davey and B. R. T. Keene. *Chem. & Ind.* 849 (1965).

[5] M. Dvolaitzky and A. S. Dreiding, *Helv. Chim. Acta* **48**, 1988 (1965).

[6] A. Schäffer and W. Ziegenbein, *Chem. Ber.* **88**, 767 (1955).

[7] E. C. Horning, V. L. Stromberg and H. A. Lloyd, *J. Amer. Chem. Soc.* **74**, 5153 (1952).

[8] R. S. Montgomery and G. Dongherty. *J. Org. Chem.* **17**, 823 (1952).

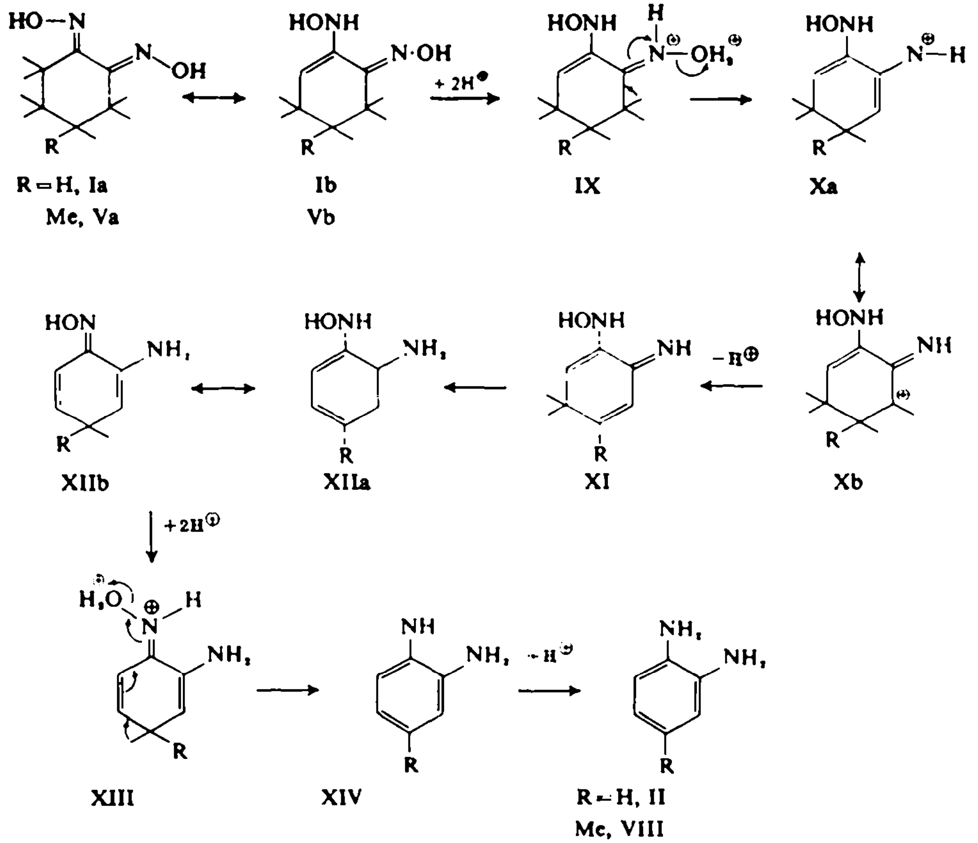
[9] I. L. Knynants and B. P. Fabrichnyi, *Doklady. Akad. Nauk. S.S.S.R.* **68**, 701 (1949).

[10] H. K. Hall, Jr., *J. Amer. Chem. Soc.* **80**, 6404 (1958).

[11] M. Rothe and R. Timler, *Chem. Ber.* **95**, 783 (1962).

[12] H. Watanabe, S. Kuwata and S. Koyama, *Chem. Pharm. Japan.* **9**, 834 (1961).

[13] L. Mamlok, *Bull. Soc. chim. Fr.* 1182 (1956).



aromatization in XIV. Conc sulfuric acid gave higher yields of *p*-phenylenediamine than if the fuming sulfuric acid was used.

As the Beckmann rearrangement of cyclohexane-1,3-dione dioxime gave unidentifiable products which were insoluble in most of the organic solvents, it is assumed that an active methylene group between oximino groups gives a reactive tautomer.

EXPERIMENTAL[14]

Materials. Conc H_2SO_4 was prepared by mixing 98% H_2SO_4 and 115% oleum to the conc of 100·3%. Cyclohexane-1,2-dione dioxime was prepared from cyclohexanone by the procedure described by West.[15] The crystals obtained were recrystallized three times from distilled water. m.p. 189·0–190·0°. Cyclohexane-1,3-dione dioxime was prepared by hydrogenation of resorcin[16] followed by treatment with hydroxylamine. m.p. 157·5°. Cyclohexane-1,4-dione dioxime was prepared by the Dieckmann reaction of diethyl succinate with sodium ethoxide,[17] followed by decarboxylation of the product by the method of Doering *et al.*,[18] and treatment of cyclohexane-1,4-dione obtained with hydroxylamine. This compd was sublimated *in vacuo*. m.p. 192°. 3-Methyl and

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[14] All were taken using a Yanagimoto heating bloc apparatus and are uncorrected. Microanalysis by Central Research Laboratories of Toyo Rayon Co., Ohtsu, Japan. IR spectra (Shimazu 27 A type); UV (Hitachi EPU-2 spectrophotometer).

[15] R. Belcher, W. Hoyle and T. S. West, *J. Chem. Soc.* 2743 (1958).

[16] H. Gilman, A. H. Blatt and E. C. Horning, *Organic Syntheses* coll. Vol. III; p. 278. Wiley, New York (1955).

[17] C. R. Hauser and B. E. Hudson, Jr., *Organic Reactions* Vol. I; p. 283. Wiley, New York (1957).

[18] W. V. E. Doering and A. A. R. Sayigh, *J. Org. Chem.* **26**, 1365 (1961).

4-methyl cyclohexane-1,2-dione dioximes were prepared by the procedure described by Banks *et al.*,[19] starting from *o*- and *p*-cresol, respectively. The m.ps of 3-methyl and 4-methyl-cyclohexane-1,4-dione dioximes are 166° and 181–183°, respectively. Nickel(II)bis(N,N′-4-methylcyclohexane-1 2-dione dioximate) was prepared by addition of nickel(II) chloride aq soln to the dioxime aq soln, and adjusting the pH around 8 by AcONa.

*Beckmann rearrangement of cyclohexane-*1,2*-dione dioxime*(I) *in conc* H_2SO_4

Into 100 ml 3-necked flask, the bottom of which was equipped with an outlet tube, provided with a stirrer and a thermometer, 44 ml conc H_2SO_4 was added and the temp was maintained at 105–110°. Compound I (20 g) was adddd in small portions with vigorous stirring during 30 min. Then 47 g I were charged continuously keeping the molar ratio I to H_2SO_4 at 10 for 1 hr.

The reaction mixture, after being stirred under the same conditions for further 30 min, was cooled and then poured into 545 g ice water. The soln was extracted with ether, and the raffinate was neutralized with saturated $Ba(OH)_2$aq to pH 8·4 under cooling, and the pptd $BaSO_4$ was filtered off *in vacuo*.

The filtrate was extracted with chf, and the remaining aq soln was treated with dry ice. After filtration, the aq soln was deionized by passing through a column of Amberlite-200(H type)-Amberlite IRA-402(OH type), and then concentrated.

(a) *Adipic acid* (III). The ether extract was dried (Na_2SO_4) and evaporated under red. press. to yield 1·1 g crude product, which was recrystallized twice from distilled water, giving pure adipic acid, 1·7%, m.p. 152·0–153·0° (undepressed by an authentic sample). IR(KBr): 1698 (C=O); UV(CH_3O): 219 mμ (ε 81·3). (Found: C, 48·96; H, 6·91. Calc. for $C_6H_{10}O_4$: C, 49·29; H, 6·90%.)

Spot test for carboxyl group was positive and a white ppt formed when 10% $(AcO)_2Hg$[20] was added to the sample soln.

(b) *o-Phenylenediamine* (II). The chf extract was dried (Na_2SO_4) and evaporated to give 9·0 g (21%) of brownish black crystals, m.p. after repeated recrystallization from MeOH–EtOH 100–102° (undepressed by an authentic sample). IR: 1596, 1505 characteristic of aromatic compds ($C \mp C$), 749 indicating *o*-substitution; 3400 and 3325 (NH_2), 1776 (CN). UV: of the free and protonated sample appeared at 230, 289, 229 and 280 μm (log ε 3·89, 3·43, 3·17 and 2·73).

The N,N′-diacetyl derivative was prepared by treating the sample with Ac_2O, m.p. 186·0–188·5°. (Found: C, 62·07; H, 6·30 N, 14·59. Calc. for $C_{10}H_{12}N_2O_2$, C, 62·61; H, 6·59; N, 14·68%.)

(c) *Amide* (IV). The raffinate extracted by both chf and ether was deionized and concentrated *in vacuo* to dryness to obtain 50 mg of white crystals; IR(KBr) 1675 cm^{-1}. The sample showed blue color in the presence of NaOCl. The hydrolysate with 6N HCl was analysed by paper chromatography (developer: n-BuOH saturated with water; coloring agent: methyl red). A spot having R_f value of 0·83 was identified as adipic acid. A portion of hydrolysate was added to 10%$(AcO)_2$ Hg aq to form a white ppt[20] m.p. 237° (dec), supposedly of mercuric adipate. Salicylaldehyde was added to another portion of hydrolysate to form a white ppt, supposedly indicating the presence of hydrazine.[21] Thus, the product obtained could be a cyclic lactam composed of adipic acid and hydrazine.

*Aromatization of cyclohexane-*1,2*-dione-dioxime* (I) *in* PPA

In a 250 ml 3-necked flask, 40 g 85% H_3PO_4 and 42 g P_2O_5 were vigorously stirred and allowed to react 100° overnight.

Cyclohexane-1,2-dione dioxime (2 g) was added in small portions during 10 min at 120–130° with vigorous stirring. Stirring was continued for further 5 min and the reaction mixture cooled to room temp and then poured into 200 g ice water. NaOH (60 g) was added under cooling. The alkaline aq soln obtained was extracted repeatedly with ether and the extract dried (Na_2SO_4) and evaporated *in vacuo* to yield 0·54 g crude crystals. Recrystallization from water gave pure *o*-phenylenediamine, yield 35%.

Aromatization of 4*-methyl cyclohexane-*1,2*-dione dioxime* (V) *in* PPA

To 117 g of PPA 2·3 g of V was added in small portions with vigorous stirring at 95–105° and stirring continued for 30 min. After cooling, the soln was poured into 300 ml ice water, neutralized

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[19] C. V. Banks, R. T. Hooker and J. J. Richard, *J. Org. Chem.* **21**, 547 (1956).

[20] E. Kroller, *Dent. Lebensm-Rundshau* **43**, 120 (1947); *Chem. Abstr.* **42**, 8164b.

[21] F. Feigel, *Spot Test in Inorganic Analysis* p. 239. Elsevier, Amsterdam (1954).

with NaOH to pH 8–9, and then extracted with chf (5 × 100 ml). The extract was evaporated to dryness to give a black tarry residue which was recrystallized from ligroin to give 0·443 g (25% yield) crystals, m.p, 86·5–88°. IR spectrum was superimposable on that of 3,4-diaminotoluene (VII). (Found: C, 68·92; H, 8·32; N, 22·36. Calc. for $C_7H_{10}N_2$: C, 68·81; H, 8·25; N, 22·98%.) On reacting with phenanthraquinone, it gave 5-methyl-1,2,3,4,dibenzophenazine, m.p. 210–216° (repeated recrystallization from benzene and then acetone). (Found: C, 85·40; H, 5·18; N, 8·89. Calc. for $C_{21}H_{14}N_2$: C, 85·68; H, 4·79; N, 9·51%.)

The same reaction was attempted by using conc and 60% H_2SO_4, H_3PO_4, benzenesulfonyl chloride in 1N NaOH, PCl_5 in ether and Beckmann's mixture. But the reaction occurred only in the case of conc H_2SO_4 with very poor yield.

Aromatization of nickel(II) *bis*(N,N′-4-*methyl cyclohexane*-1,2-*dione dioximate*) (VIII) *in* PPA

In a 100 ml 3-necked flask, PPA (80 g) at 95–105° was added with vigorous stirring to VIII (1·92 g in small portions) and the mixtures allowed to react for 1 hr. The soln was then poured into ice water, neutralized and extracted with chf to give 0·18 g (14·7%) pure 3,4-diaminotoluene.

Beckmann rearrangement of cyclohexane 1,4-*dione dioxime* (XIV) *in conc* H_2SO_4

To 55·2 g (0·548 mole) conc H_2SO_4 in a 100 ml 3-necked flask at 80–95°, XIV (8·0 g; 0·0562 mole) was added in small portions with vigorous stirring. The reaction mixture was heated at 100° for 50 min. After cooling, the soln was poured into 200 g ice water and insoluble products were filtered off. The filtrate was extracted with ether (a) and then the aq soln was divided into two portions (b) and (c).

(a) *Succinic acid* (XIX). The ether extract was dried (Na_2SO_4) and evaporated *in vacuo* to dryness yielding white crystals m.p. 182–183° identical (IR, R_f and m.m.p.) with succinic acid.

(b) p-*Phenylenediamine* (XVIII). Half of the aq soln was neutralized with NaOH to pH 8·0. After filtering off the Na_2SO_4, the filtrate was extracted with ether, and the extract concentrated to dryness to give 1·12 g *p*-phenylenediamine by the indamine test[11] and paper chromatography (developer: MeOH-amyl alcohol-benzene-water/4:2:2:2; coloring agent/vanillin in HCl, R_f 0·66). *p*-Phenylenediamine was separated from the residue by treating with picryl chloride to give N,N′-bis(2,4,6-trinitrophenyl)-p-phenylenediamine (9·3%). UV(acetone). 415 mμ (log ε 4·27). The C–NO stretching frequencies appeared at 1615 and 1325 cm^{-1}. (Found: C, 41·03; H, 2·46; O, 35·52; N, 20·65; Calc. for $C_{18}H_{10}N_8O_{12}$: C, 40·77; H, 1·90; O, 36·20; N, 21·13%.)

(c) 1,5-*Diaza*-4,8-*dioxocyclooctane*(XV). The second half of the aq soln was neutralized with $Ba(OH)_2$ to pH 11 and the ppt filtered off *in vacuo*. The excess $Ba(OH)_2$ was removed by addition of dry ice to form $BaCO_3$.

The filtrate was deionized by Amberlite-200 (H-type)-Amberlite IRA-402(OH type), and then evaporated to dryness. The residue was recrystallized from EtOH to give 0·16 g (2%) granular white crystals m.p. 298–300° (lit.[10,11] 298°). The amide I band, and amide II band appeared at 1660 and 1575 cm^{-1}, respectively. The hydrolysate was confirmed as β-alanine by paper chromatography.

Beckmann rearrangement of cyclohexane 1,4-*dione dioxime* (XIV) *in oleum*

The dioxime (7·8 g) was reacted in 80·7 g 15% oleum at 95–105° for 30 min and the soln was poured into 200 g ice water, yielding *p*-phenylenediamine and 1,5-diaza-4,8-dioxocyclooctane (1, 2% and 8·7%) respectively.

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[11] F. Feigl, *Spots Tests in Organic Analysis* p. 405. Elsevier, Amsterdam (1954).