mm.), $n^{21}\mathrm{D}$ 1.4416, $n^{18}\mathrm{D}$ 1.4430; reported b.p. 112–114° (12 mm.), $n^{21}\mathrm{D}$ 1.441[20]; b.p. 121° (23 mm.), $n^{18}\mathrm{D}$ 1.4467.[8]

The bis-3,5-dinitrobenzoate prepared as in the above case crystallized from acetone–methanol; m.p. 156.3–157°.

Anal. Calcd. for $C_{22}H_{22}O_{12}N_4$: C, 49.44; H, 4.15; N, 10.48. Found: C, 49.77; H, 4.32; N, 10.30.

SALT LAKE CITY 12, UTAH

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[20] J. E. Dubois, *Ann. chim.* (*Paris*), **6**, 406 (1951).

[CONTRIBUTION FROM THE CHEMICAL RESEARCH INSTITUTE OF NON-AQUEOUS SOLUTIONS, TOHOKU UNIVERSITY]

The Beckmann Rearrangement in Liquid Sulfur Dioxide. II.[1] Rearrangement by Halogen

BY NIICHIRO TOKURA, RYUZO ASAMI AND RITSURO TADA

RECEIVED JUNE 27, 1956

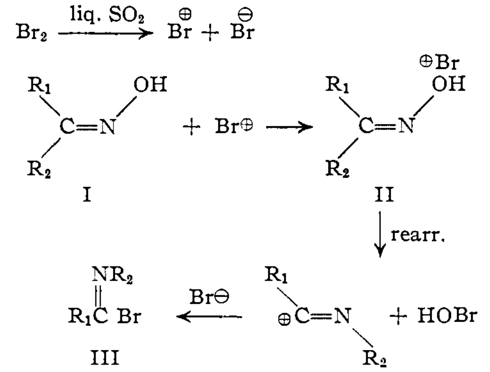
The Beckmann rearrangement of ketoximes may be effected by bromine and iodine in liquid sulfur dioxide at room temperature. Chlorine and sulfuryl chloride are without effect, but the addition of a small quantity of bromine (0.02:1 mole ratio) to these reagents leads to rearrangement. The oximes studied were those from cyclohexanone, cyclopentanone, acetophenone and benzophenone; in the case of aromatic oximes the reaction products were brominated or chlorinated amides. A possible mechanism is discussed.

Previous work has shown that the Beckmann rearrangement may be carried out in liquid sulfur dioxide at room temperature with sulfur trioxide,[1,2] with thionyl chloride and with a variety of phosphorus compounds.[1] It now has been found that the rearrangement may also be effected in sulfur dioxide solution by bromine, by iodine and by chlorine or sulfuryl chloride in the presence of small amounts of bromine (1:1:0.02 mole ratio for oxime:chlorine:bromine). Chlorine and sulfuryl chloride did not induce rearrangement when they were used without added bromine.

Rearrangements of the oximes of cyclohexanone, cyclopentanone, acetophenone and benzophenone were studied under varying conditions. Table I contains the results of experiments with cyclohexanone oxime in liquid sulfur dioxide. The best results were obtained with a 1:1 mole ratio of bromine to oxime (58 and 64% yield of ε-caprolactam for reaction periods of 1 and 24 hr., respectively) and with chlorine and sulfuryl chloride containing a small amount of bromine (67–72% yield of lactam). The yield of amide was not increased by increasing amounts of bromine, but a decrease in the bromine to oxime ratio to 0.5:1 decreased the yield of amide to 39%.

The bromine procedure (1:1 mole ratio, 1 hr. at 20°) and the chlorine–bromine procedure (1:1:0.02 mole ratio for oxime:chlorine:bromine, 1 hr. at 20°) were applied to the oximes of cyclopentanone, acetophenone and benzophenone. The results are given in Table II. Amides from acetophenone oxime and benzophenone oxime were halogenated under these conditions. Halogenation evidently occurred after the rearrangement reaction, since the products from benzophenone oxime were those to be expected from the halogenation of benzanilide.

The mechanism of the rearrangement is thought to be



This mechanism requires a 1:1 mole ratio of bromine to oxime for complete reaction. The formation of an amide from the intermediate III may occur during the reaction or at the time of addition of water to the reaction mixture. An alternate

TABLE I

ACTION OF HALOGEN ON CYCLOHEXANONE OXIME IN LIQUID SO_2[a]

Reagent	Molar ratio of oxime to halogen	Lactam formed, yield, %
Br_2,H_2O[b]	1:1	0
Br_2,H_2O[c]	1:1	0
Br_2	1:0.5	39.2[e]
Br_2	1:1	58.0
Br_2	1:1.4	59.2
Br_2[d]	1:1	64.0
I_2	1:1	34.0
Cl_2	1:1	0
SO_2Cl_2	1:1	0
Cl_2,Br_2	1:1:0.1	72.4
Cl_2,Br_2	1:1:0.02	67.2
Cl_2,Br_2	1:1:0.02	66.8
Cl_2,I_2	1:1:0.1	12.4
SO_2Cl_2,Br_2	1:1:0.02	70.4

[a] Reaction carried out at 20° for 1 hr., with 25 g. (0.22 mole) of the oxime and 200 ml. of liq. SO_2. [b] Molar ratio of bromine to water was 1:2. [c] Molar ratio of bromine to water was 1:1. [d] Reaction carried out at 20° for 24 hr. [e] 78.4% on the basis of bromine used.

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[1] For the first paper of this series, see N. Tokura, R. Asami and R. Tada, *Sci. Reports Research Inst., Tohoku Univ.*, **8**, 149 (1956).

[2] German Patent 858,397 (1952); *C. A.*, **48**, 12810 (1954); British Patent 732,899 (1955); *C. A.*, **50**, 5738 (1956).

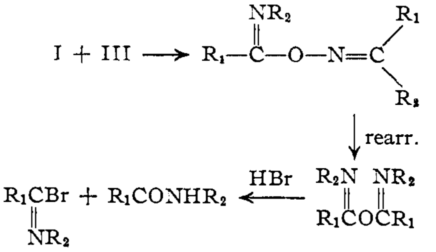
TABLE II

ACTION OF HALOGEN ON KETOXIMES IN LIQUID SO_2[a]

Oxime of	Reagent	Molar ratio of oxime to halogen	Rearrangement product	Yield, %
Cyclopentanone	Br_2	1:1	δ-Valerolactam	37.2
Acetophenone	Br_2	1:1	*p*-Bromoacetanilide	32.0
Benzophenone	Br_2	1:1	N-Benzoyl-*p*-bromoaniline	51.6
Cyclopentanone	Cl_2,Br_2	1:1:0.02	δ-Valerolactam	52.2
Acetophenone	Cl_2,Br_2	1:1:0.02	Acetanilide	32.5
			p-Chloroacetanilide	22.3
Benzophenone	Cl_2,Br_2	1:1:0.02	N-Benzoyl-*o*-chloroaniline	28.4
			N-Benzoyl-*p*-chloroaniline	51.7

[a] Reaction carried out at 20° for 1 hr. in liquid SO_2.

possibility also must be considered. From the work of Stephen and Staskun,[3] it is likely that III and the oxime might also react to form an intermediate in the Stephen–Staskun proposal for the Beckmann rearrangement. Thus



An advantage of this mechanism is the fact that the amide is represented as a direct product of the rearrangement condition. In this case the amide would be available for halogenation by the HOBr resulting from II → III.

The inability of chlorine to bring about rearrangement of an oxime under these circumstances may be due to a failure to form Cl.$^\oplus$ The catalytic effect of bromine, when used with chlorine, can be ascribed to the regeneration of Br$^\oplus$ in the following way

$$Cl_2 + HOBr \longrightarrow ClBr + HOCl$$

$$ClBr \xrightarrow{\text{Liq. } SO_2} \overset{\ominus}{Cl} + \overset{\oplus}{Br}$$

The effect of bromine and water on the rearrangement reaction was also investigated. It is known that the reaction of bromine and water in liquid sulfur dioxide is[4]

$$Br_2 + 2H_2O + SO_2 \longrightarrow 2HBr + H_2SO_4$$

The hydrogen bromide remains in solution, but the sulfuric acid forms an insoluble lower layer. A mixture prepared in this way was not effective in bringing about the rearrangement of cyclohexanone oxime.

From the fact that the hydroxyl of the oxime undergoes reaction with a halogen in liquid sulfur dioxide, the hydroxyl of a substituted alcohol $-\overset{|}{\underset{|}{C}}-OH$ should also undergo substitution with a halogen by the same procedure. Data on such a reaction will be published at later date.

Acknowledgment.—The authors wish to thank a reviewer for his help and Emeritus Prof. Dr. R. Hara for his interest and encouragement in this investigation. The authors are indebted to Miss Y. Endo for the microanalyses, to the Befu Chemical Industries Co. for donation of the liquid sulfur dioxide used in this research and to the Ministry of Education of Japan for a grant.

Experimental

Reagents.—Oximes were made by reaction of the appropriate ketone and hydroxylamine according to the references indicated; the oximes were cyclohexanone oxime[5] (m.p. 89–90.5°), cyclopentanone oxime[6] (m.p. 56.5–57°), acetophenone oxime[7] (m.p. 59.5–60.5°) and benzophenone oxime[8] (m.p. 141.5–142°).

Liquid sulfur dioxide was used as a solvent. Commercial material was used after filtration. It was found unnecessary to redistil the liquid or to dry it with sulfuric acid or phosphorus pentoxide.

The chlorine was distilled before use. Bromine was dried with sulfuric acid in the usual way. The iodine was washed with water and dried before use. The sulfuryl chloride was distilled (b.p. 66.5–67.5° (760 mm.)).

Apparatus and General Procedure.—Glass pressure vessels (300-ml. capacity) equipped with metal joints were used. Liquid sulfur dioxide was added to the oxime, with ice-cooling of the vessel, and a solution of the halogen or other reagents in sulfur dioxide was then added. Reverse addition was used for iodine reactions, since this material is sparingly soluble in sulfur dioxide. Chlorine solutions were best prepared by the addition of chlorine to sulfur dioxide.

Rearrangement of Cyclohexanone Oxime (Table I).—To a solution of 25 g. (0.22 mole) of cyclohexanone oxime in 100 ml. of sulfur dioxide there was added 100 ml. of sulfur dioxide containing the reagents indicated in Table I in various molar ratios. After the indicated time at 20° (usually 1 hr.), water was added with chilling and the solvent was allowed to evaporate. The residue was neutralized with 25% sodium hydroxide solution, and the products were extracted with chloroform. The chloroform was removed (reduced pressure) and the mixture was distilled under reduced pressure to yield cyclohexanone (b.p. 55–65° (35–36 mm.)), unchanged oxime (b.p. 95–115° (10–11 mm.)) and ε-caprolactam (b.p. 120–130° (7–8 mm.)). The ε-caprolactam was recrystallized from ether to yield a product with m.p. 67–68°. This was hydrolyzed with 15% sodium hydroxide solution and benzoylated to ε-benzoylaminocaproic acid,[9] m.p. 80–80.5°, for identification purposes (a mixed m.p. with an authentic sample was not depressed).

Yields obtained with a variety of reagents and conditions are in Table I.

Rearrangement of Ketoximes (Table II).—A solution of 35.5 g. (0.22 mole) of bromine in 100 ml. of sulfur dioxide was added to a solution of 22 g. (0.22 mole) of cyclopentanone oxime in 100 ml. of sulfur dioxide. After 1 hr. at 20°, the reaction mixture was treated as in the previous set of experiments. From the chloroform extract there was obtained by distillation 8.2 g. (37.2%) of δ-valerolactam, collected at 130–140° (15–16 mm.). This material, m.p. about 30°, was converted for identification into 1,3-dioxo-2-isoindolinevaleric acid[10] by treatment with phthalic anhydride; the m.p. and mixed m.p. with an authentic sample was 117–118°.

When this reaction was repeated with a chlorine–bromine mixture (1:0.02 mole ratio), the yield was 52.2% of δ-valerolactam, collected at 130–140° (15–16 mm.) and identified as before.

For acetophenone oxime, the reaction was carried out in the following way. A solution of 16 g. (0.1 mole) of bromine in 50 ml. of sulfur dioxide was added to a solution of 13.5 g.

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[3] H. Stephen and B. Staskun, *J. Chem. Soc.*, 980 (1956).

[4] J. Ross, J. H. Percy, R. L. Brandt, A. I. Gebhart, J. E. Mitchell and S. Tolles, *Ind. Eng. Chem.*, **34**, 924 (1942).

[5] E. W. Bousquet, *Org. Syntheses*, **11**, 56 (1931).

[6] S. W. Fox, M. S. Dunn and M. P. Stoddard, *J. Org. Chem.*, **6**, 411 (1941).

[7] A. Janny, *Ber.*, **15**, 2781 (1882).

[8] A. Lachman, *Org. Syntheses*, **10**, 10 (1930).

[9] A. Galat, THIS JOURNAL, **69**, 86 (1947).

[10] M. Taniyama, T. Takata and K. Sayama, *J. Chem. Soc. Japan., Ind. Sect.*, **59**, 545 (1956).

(0.1 mole) of acetophenone oxime in 50 ml. of sulfur dioxide. After the reaction period, the sulfur dioxide was removed as usual and the residue was treated with 25% sodium hydroxide solution. The products were extracted with ether; the ether solution was dried and evaporated to yield 14.8 g. of material. Trituration with ether gave 7.9 g. of soluble material and 6.9 g. of colorless residue, m.p. *ca.* 155°, which was recrystallized from benzene to give a crystalline product with m.p. 164–165.5°, not depressed on mixture with authentic *p*-bromoacetanilide.

When the reaction was repeated on the same scale with a chlorine–bromine mixture, a yield of 14.5 g. of crude mixed products was obtained. This was triturated with benzene–ligroin (6.3 g. was soluble) to give 7.9 g. of colorless residue. Fractional crystallization from water gave 4.4 g. of material melting at about 100° and 3.8 g. of material melting at about 165°. Each fraction was crystallized from benzene; the products were identified as acetanilide (m.p. and mixed m.p. 113–114°) and *p*-chloroacetanilide (m.p. and mixed m.p. 171–172.5°).

The reaction with benzophenone oxime (19.7 g., 0.1 mole) was carried out in the usual way in 100-ml. total volume of sulfur dioxide. The yield of 18.7 g. of crude product was triturated in ether (4.4 g. of soluble material) to give 14.3 g. of orange powder, m.p. 201–202°. The m.p. was not depressed on mixture with authentic N-benzoyl-*p*-bromoaniline.

When a chlorine–bromine mixture was used with 0.1 mole of benzophenone oxime, crude product amounted to 20.3 g. This was triturated with benzene, and the benzene solution yielded 6.6 g. of N-benzoyl-*o*-chloroaniline, m.p. and mixed m.p. 99–101° after recrystallization from ethanol. The benzene-insoluble residue was fractionally crystallized to give 12 g. of N-benzoyl-*p*-chloroaniline, m.p. and mixed m.p. 187–188.5°, and an unidentified material (1.7 g.) with m.p. 150–152°.

Satisfactory nitrogen analyses were obtained for all reaction products.

Reactions with Bromine–Water Mixture.—When a bromine-water mixture was used in sulfur dioxide with cyclohexanone oxime, a rearrangement did not occur (Table I). Cyclohexanone and cyclohexanone oxime were recovered. For the reactions in Table I, the recovery of oxime was 74.0 and 87.6%.

SENDAI, JAPAN

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DIVISION, POLYMER CORPORATION LTD.]

The Synthesis and Identification of Block Polymers of Butadiene and Styrene

BY R. J. ORR AND H. LEVERNE WILLIAMS

RECEIVED NOVEMBER 21, 1956

A method of synthesizing polymeric dihydroperoxides in which the hydroperoxy groups are terminal has been evolved. The monomers are polymerized in emulsion at 12.8° using sufficiently large quantities of complexed iron(II) and *p*-diisopropylbenzene dihydroperoxide that mutual termination is dominant. The molecular weight of the polymeric dihydroperoxide is controlled by adjusting the emulsifier, the dihydroperoxide and the iron(II) sulfate concentrations. The residual hydroperoxide group on the polymer is protected from reaction by the short residence time in the aqueous phase. Such polymers after purification will initiate polymerization of a second monomer. The iodine monochloride adduct of butadiene–styrene copolymers is insoluble in carbon tetrachloride for high-butadiene polymers and soluble for low-butadiene polymers. This permitted verification that the polymers produced by initiating styrene polymerization with polybutadiene dihydroperoxide were not mixtures of polystyrene and polybutadiene but were composed of chemically linked blocks of polymers of the two compositions. This was supported by fractionation experiments which indicated that some bound styrene could not be extracted after cross-linking such a polymer. Evidence is presented that such results do not arise from chain transfer.

Introduction

Active interest in the field of block and graft polymers is comparatively recent, stimulated by the potential economic value of some novel product. While methods of grafting are numerous, since they depend only on placing side chains randomly along the main chain, the methods of forming block polymers are few due to the restriction on the location of the points of union of the blocks in the molecule. Several reviews[1–3] summarize methods. The methods have the defect that if they are simple and commercially feasible they offer little control over the structure of the final polymer. The problem of exerting control over the process and product seems to be the major difficulty.

It is important to establish by analytical methods the structure of the polymer postulated from kinetic reasoning. Fractionation of the product of the reaction may be tedious, and success in separating differing polymers depends on the difference in solubilities of the polymers. There is little difference between the solution properties of polybutadiene and polystyrene, so that this approach offers little promise, although some workers report successful fractionations of similar polymer mixtures.[4]

During the course of the study of the decomposition of hydroperoxides by iron(II), *p*-diisopropylbenzene dihydroperoxide was used.[5] This gave a free radical which underwent little side reaction relative to reaction with monomer. Considering the theories of emulsion polymerization as outlined by Harkins[6] and Smith and Ewart[7] suggested that sufficiently rapid decomposition of hydroperoxide might result in appreciable amounts of mutual termination according to the mechanism

$$\mathrm{HOOROOH(aq)} + \mathrm{Fe(II)} \longrightarrow \mathrm{HOORO\cdot(aq)} + \mathrm{Fe(III)}$$

$$\mathrm{HOORO\cdot(aq)} + \mathrm{M(aq)} \longrightarrow$$

$$\mathrm{HOOROM\cdot(aq)} \xrightarrow{(n-1)\mathrm{M}} \mathrm{HOOROM}_n\mathrm{\cdot(oil)}$$

$$\mathrm{HOOROM}_n\mathrm{(oil)} + \mathrm{pM(oil)} \longrightarrow (\mathrm{HOOROM}_{n+p})\mathrm{(oil)}$$

$$\mathrm{HOOROM}_n\mathrm{(oil)} + \mathrm{HOOROM}_{n+p}\mathrm{(oil)} \longrightarrow \mathrm{HOOROM}_{2n+p}\ \mathrm{OROOH}$$

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