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THE BECKMANN REARRANGEMENT. IV. STUDY OF THE RATES OF SOME ALIPHATIC AND ALICYCLIC OXIMES

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Considerable data have been accumulated concerning the rates of rearrangement of aromatic oximes, particularly of substituted acetophenone oximes (1–3). The purpose of the present work was to extend the study to aliphatic types.

Very little kinetic work seems to have been done on the rearrangement of aliphatic oximes. In fact, the only reports which were found concerned the industrially important compound, cyclohexanone oxime. Wichterle and Rocek (4) measured the rates of rearrangement of this oxime dissolved in a mixture of ϵ-caprolactam, the rearrangement product, and varying concentrations of oleum: the activation energy was found to be constant (24.8 ± 0.4 kilocalories) between 30–80% oleum concentration, the increase in rate being reflected in the frequency factor (10^{13} to $10^{15.5}$ sec^{-1}). They also reported that the reaction rate at 30° is first order with respect to the oxime in a mixture of 15 g. of oleum, 14 g. of caprolactam, and 1 g. of oxime (5). Rocek and Bergl (6) stated that the rate of rearrangement of cyclohexanone oxime is independent of the oleum concentration within the range 5–10%. Apparently, all these studies were carried out by means of the colorimetric determination of the blue-colored 1-chloro-1-nitrosocyclohexane obtained from the oxime by chlorination. Other investigators have been more interested in the products of the rearrangement than in the rates (*e.g.*, 7, 8). The lack of interest in rates has possibly resulted in rather uncontrolled methods of synthesis of amides from oximes. The usual laboratory method is to dissolve the oxime in sulfuric acid and heat until a reaction takes place as noted by heat evolution (*e.g.*, 7, 9). The study of rates of rearrangement not only suggests more satisfactory conditions for the reactions but also permits one to compare the effects of substituents—a study which may lead to a better understanding of the mechanism of this reaction and of similar reactions. In addition, the rearrangement products of alicyclic oximes are of interest as potential polymer sources. For these reasons the study of the rates of rearrangement of some aliphatic and alicyclic ketoximes has been undertaken.

The previously used analytical method for following the rates of rearrangement of an oxime in sulfuric acid has consisted of gravimetric determination of the 2,4-dinitrophenylhydrazone of the ketone obtained by hydrolysis of the oxime (1–3). This procedure was unsatisfactory for the determination of the lower molecular weight ketoximes because of appreciable solubility of the 2,4-dinitrophenylhydrazones in water and in dilute acid. A new procedure was

[1] Taken in major part from the Ph.D. thesis of Paul T. Scott, Vanderbilt University, 1954.

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TABLE I

RATE CHARACTERISTICS OF THE REARRANGEMENT OF ALIPHATIC OXIMES IN SULFURIC ACID

Oxime[a]	t, °C.	$k^b \times 10^3$	$t^c_{\frac{1}{2}}$	E_A^d	ΔS^e
Acetone	90.66	1.17 ± .01	592	30.1	0.6
	95.82	2.10 ± .03	330		
	98.43	2.81 ± .11	247		
	107.52	7.43 ± .02	93		
	111.74	11.5 ± .0	60		
Diethyl ketone	50.90	1.48 ± .01	468	25.4	−3.4
	60.31	4.49 ± .07	154		
	70.47	13.9 ± .3	50		
Diisopropyl ketone	21.86	2.36 ± .01	294	23.5	−1.1
	30.66	7.55 ± .04	92		
	40.90	26.9 ± .1	26		
Diisobutyl ketone	40.43	1.47 ± .00	471	25.7	0.0
	50.59	5.34 ± .06	130		
	60.39	17.3 ± .1	40		
Cyclopentanone	51.00	1.17 ± .01	592	26.9	0.9
	60.92	4.09 ± .04	169		
	69.90	11.8 ± .1	59		
Cyclohexanone	30.00	0.557 ± .005	1244	24.7	−2.2
	40.90	2.31 ± .04	300		
	50.90	7.85 ± .12	88		
Cycloheptanone	40.82	0.51 ± .01	1344	26.3	−0.1
	51.03	1.92 ± .06	373		
	60.62	6.20 ± .10	110		

[a] Concentration: 0.002 mole in 20 ml. of 94.5% H_2SO_4 (Merck). [b] True k in reciprocal minutes; see Experimental Section, IV. [c] Half-life in reciprocal minutes. [d] Activation energy in kilocalories. [e] Entropy of activation at 50.9°.

therefore developed which proved to be quite superior to the gravimetric one and which, indeed, shows considerable promise as a general method for the determination of any carbonyl compound.[3] The new method is a colorimetric determination based on favorable differences of partition coefficients of the reagent, 2,4-dinitrophenylhydrazine, and of the 2,4-dinitrophenylhydrazone between the two phases, dilute aqueous acid and carbon tetrachloride. The hydrazine reagent is almost completely insoluble in carbon tetrachloride while the hydrazone is very soluble in this solvent. Any deviation from the above rather broad statement of principle is compensated for by the use of calibration curves made with known amounts of oxime under conditions and in concentrations identical to the determination during the rate runs. A detailed description of the method is given in the Experimental Section, together with pertinent comments on practical details.

The new analytical procedure made it possible to extend the study to rates

[3] Added in press. Johnson and Scholes, *Analyst*, **79**, 217 (1954) have recently proposed a colorimetric determination of acetaldehyde-2,4-DNH. They use perchloric acid to hold the reagent in the aqueous phase and develop the color of the 2,4-dinitrophenylhydrazone in the carbon tetrachloride phase with alkali.

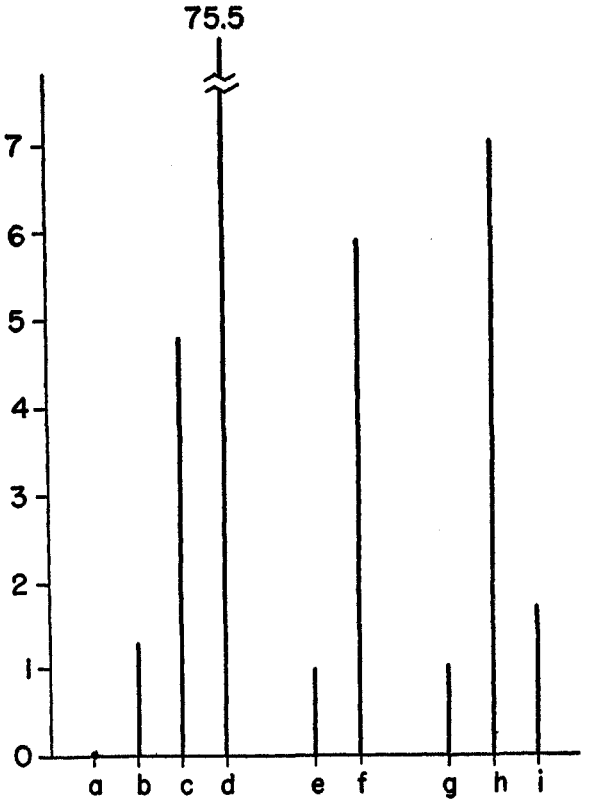


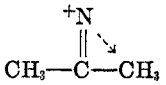
FIGURE 1. RATES OF REARRANGEMENT OF OXIMES RELATIVE TO ACETOPHENONE OXIME. (a) Acetone oxime. (b) Diethyl ketoxime. (c) Diisobutyl ketoxime. (d) Diisopropyl ketoxime. (e) Acetophenone oxime (2). (f) Benzophenone oxime (2). (g) Cyclopentanone oxime. (h) Cyclohexanone oxime. (i) Cycloheptanone oxime. Acetophenone oxime rate, actual $k = 1.127 \times 10^{-3}$ reciprocal minutes, is taken as 1.0. All rates compared at 50.9°.

of rearrangement of symmetrical aliphatic ketoximes and of alicyclic ketoximes. The oximes were rearranged under conditions similar to those of previous studies (1–3) in which about 0.001 mole of oxime was dissolved in 10 ml. of concentrated sulfuric acid and permitted to rearrange at known temperatures. At certain intervals aliquots were removed and analyzed for oxime content by the colorimetric method. The rates were all first order reactions with respect to the oxime. The Arrhenius plots of log k *vs.* reciprocal temperature were linear for all oximes but are not illustrated in this paper. The results are recorded in Table I, and a visual comparison of results is given in Figure 1.

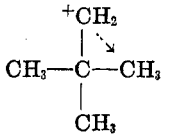
The results may possibly be interpreted as follows in the discussion. The aromatic oximes have an unusual mode of rearrangement, probably involving *p*-quinoid structures in the transition complex (3). This mode of rearrangement is not available to aliphatic oximes. Rather, direct attack of an electron-deficient nitrogen atom must be made on a saturated carbon center[4] in a manner similar

[4] The susceptibility of the alkyl group to attack by the electron-deficient nitrogen atom

to the attack of a carbonium ion on a saturated carbon center in the Wagner-Meerwein rearrangement:



Beckmann Rearrangement



Wagner-Meerwein Rearrangement

Acetoxime should therefore rearrange more slowly than aromatic oximes. Figure 1 shows that the rate of rearrangement of acetoxime (a) at 50.9° is negligible, and Table I shows that measurable rates for this compound are obtained only in the neighborhood of 100°.

On the other hand, other aliphatic oximes have groups attached directly to the carbon atom under attack by the electron-deficient nitrogen atom. With increasing substitution of alkyl groups, such as is found in the series: diethyl (b), diisobutyl (c), and diisopropyl (d) ketoximes, the rates should therefore increase considerably because of short distance electron-release and should also increase in the order given. Figure 1 substantiates this view; the rates increase by the factors, 1.3, 4.8, and 75.5, for the oximes given respectively above. The factors are in the order of the inductive effects of the groups. However, the magnitude of the factors is not a true comparison of group effects because the unattacked group of the oxime was altered at the same time. In other words, symmetrical ketoximes were studied rather than ketoximes with a single unattacked group such as the series, methyl alkyl ketoximes.

It was anticipated that the sterically hindered diisopropyl ketoxime would have a large negative entropy of activation because of the restricted nature of the reaction path. It was found (Table I), however, that the entropy of activation was essentially the same as that of other oximes.

The rate sequence of cyclopentanone, cyclohexanone, and cycloheptanone oximes (Figure 1: g, h, and i) is apparently an excellent confirmation of the generalization of Brown, Brewster, and Shechter (10). They state that the introduction of an exo double-bond stabilizes the cyclopentane and destabilizes the cyclohexane ring system by altering the number and degree of unfavorable conformations. Cyclohexanone oxime should tend to relieve the more unfavorable conformations of its ring system by rearrangement to an expanded ring system; cyclopentanone oxime should have less tendency to undergo this change. These effects are evident from Figure 1, and it can be further inferred from Figure 1 that the cycloheptanone oxime ring system does not have to the same degree the unfavorable conformations of the ring system of cyclohexanone oxime.

is usually referred to as the "migratory aptitude" of the group. The latter term is misleading. The group probably does not move to the nitrogen atom. It seems more likely that the active center, the electron-deficient nitrogen atom, attacks the alkyl group. If the attack begins before electron-deficiency is fully established, the group *trans* to the hydroxyl group of the oxime would be attacked. This concept seems more feasible than the "push-pull" concept (1).

The rate data of cyclohexanone oxime have been utilized in developing two methods of synthesis of ϵ-caprolactam. Both methods appear to be superior to the *Organic Syntheses'* method (9) and are given in detail in the Experimental Section.

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EXPERIMENTAL

I *Ketone derivatives.* The oximes were made by the method of Pearson and Bruton (3) and were stored in a desiccator over solid potassium hydroxide. The aliphatic oximes appear to be much more stable in storage than the aromatic oximes (3). The 2,4-dinitrophenylhydrazones (2,4-DNPH) were made by the method of McElvain (11). If no reference is given to the reported melting point, the melting point is identical with that reported by McElvain (11). All melting points are corrected, and boiling points are uncorrected.

Acetone. The *oxime*, after sublimation at 2 mm. pressure, was obtained as transparent prisms, m.p. 59–59.5°. The *2,4-DNPH* was obtained as long, yellow-orange plates, m.p. 127–128°.

Diethyl ketone. The *oxime*, after fractionation in a 10-inch carborundum column, was obtained as a colorless, viscous oil: b.p. 87° at 35 mm.; n_D^{25} 1.4437 and constant among four fractions. McElvain (11) and Shriner and Fuson (12) report this oxime to be crystalline (m.p. 69°), but Timmermans (13) reports it to be a liquid: b.p. 165° at 760 mm., f.p. −22.9°, and n_D^{24} 1.4435. The *2,4-DNPH* was obtained as oblong, bright orange plates, m.p. 161–162°.

Diisopropyl ketone. The *oxime*, after fractionation, was obtained as a waxy solid of camphoraceous odor: m.p. 34°; b.p. 91.5° at 21 mm.; $n_D^{25.4}$ 1.4447 (constant in 4 out of 6 fractions). It was not profitable to crystallize this oxime because of its low melting point. The *2,4-DNPH*, recrystallized from methylcyclohexane, was obtained as soft, orange crystals, m.p. 92.5–93.5°.

Diisobutyl ketone. The *oxime*, after fractionation, was obtained as a colorless oil of fresh, pear-like odor: b.p. 74° at 2 mm., n_D^{25} 1.4458. The five fractions collected varied in refractive index from 1.4456 to 1.4459. Both McElvain (11) and Shriner and Fuson (12) are in error in reporting this compound to be a solid (m.p. 210°). The *2,4-DNPH*, recrystallized from methylcyclohexane, was obtained as orange plates with bronze luster, m.p. 91–92.5°.

Cyclopentanone. The *oxime*, after sublimation at 2 mm. pressure, was obtained as dense, transparent prisms, m.p. 56.5–57.5°. The *2,4-DNPH*, after recrystallization from a mixture of methylcyclohexane and ethyl acetate, was obtained as yellow-orange plates, m.p. 145.5–146°.

Cyclohexanone. The *oxime*, after sublimation at 2 mm. pressure, was obtained as transparent prisms, m.p. 89–90°. The *2,4-DNPH* was obtained as yellow-orange plates, m.p. 161–162°.

Cycloheptanone.[5] The *oxime* was obtained as a viscous, colorless oil: b.p. 91° at 2 mm.; n_D^{25} 1.5007; reported (14) b.p. 150° at 20 mm. The *2,4-DNPH* was obtained as small, yellow crystals, m.p. 148–149°.

II *Analytical procedure.* The procedure for analysis of cyclopentanone oxime is typical and is therefore given in detail. A stock solution of cyclopentanone oxime was prepared by dissolving 0.3434 g. (3.466 millimole) of oxime in 49.700 g. of water;[6] as a check, a second stock solution was usually prepared at the same time. Known volumes of stock solution were added from a burette to each of eight different two-ounce, screw-cap bottles. The

[5] The authors are indebted to Dr. Don C. Iffland, W. Virginia University, for the cycloheptanone used in this investigation.

[6] All measurements involving the oxime dissolved in water or in sulfuric acid were made on a mg. per g. basis rather than mg. per ml. basis in order to increase accuracy.

bottles were weighed accurately before and after addition; they contained Teflon gaskets, although aluminum foil gaskets could be used for single runs. The weight of stock solution in each bottle ranged from 2.9800 g. to 1.5018 g. From another burette, enough water was added to make the total volume of the water in each bottle 23.0 ml. Then, 2.0 ml. of concentrated sulfuric acid (by means of a pipette) and 0.300 g. of 2,4-dinitrophenylhydrazine were added to each bottle. (The amount of hydrazine is sufficient to more than saturate both the aqueous acid phase and the carbon tetrachloride phase to be added later.) The bottles were sealed tightly with screw-caps and were placed in a bath at 50° for approximately 20 hours with occasional swirling (the 2,4-dinitrophenylhydrazone precipitated so rapidly that the above digestion period could probably be shortened). The bottles were then removed from the bath and cooled to room temperature. After the addition of 25.0 ml. of carbon tetrachloride to each bottle, the bottles were again recapped, shaken very thoroughly, and allowed to stand at room temperature for about 12 hours. About half the volume of the carbon tetrachloride layer was then removed from each bottle by means of a pipette and filtered. Exactly 1.0 ml. of the yellow-colored filtrate was diluted with 50.0 ml. of carbon tetrachloride. (The high dilution factor necessitates accurate measurement of the 1.0 ml. of colored filtrate. This was done by using the same 1 ml. pipette for aliquoting all samples and by rinsing this pipette several times with the colored filtrate to be aliquoted.) A 25.0-ml. aliquot of this solution was then diluted further with 25.0 ml. of carbon tetrachloride by means of a pipette. The optical density of this solution was determined at a wave-length of 410 mμ using a Beckmann Model DU spectrophotometer. A blank carbon tetrachloride solution, containing none of the oxime but which had otherwise been treated exactly as the other samples, was used in the reference cell of the instrument. The optical density was found to be a straight line function of the concentration of the oxime over the range of concentrations that were used; mg. of oxime *vs.* optical density: 10.32, 0.467; 12.30, 0.562; 13.58, 0.619; 15.13, 0.679; 16.46, 0.744; 17.88, 0.795; 19.16, 0.842; 20.48, 0.908. In this case, the optical density was used in place of the concentration in order to obtain the rate constant.

III *Further comments on the analytical procedure.* Cycloheptanone oxime and diisopropyl and diisobutyl ketoximes were insoluble in water. The stock solutions of these ketoximes were each made with approximately 5 ml. of concentrated sulfuric acid diluted to a volume of 50 ml. with water. Under these conditions the diisopropyl ketoxime underwent some rearrangement as noted by the diminution of the calibration curve with time. The calibration curve of this compound was therefore completed as soon as possible. For each fraction of a milliliter of sulfuric acid used in the stock solution aliquots, this same fraction was subtracted from the 2.0 ml. of sulfuric acid added to the digestion samples. In other words, in all digestions 23.0 ml. of water, 2.0 ml. of sulfuric acid, and 0.300 g. of 2,4-dinitrophenylhydrazine were contained in each screw-cap bottle.

Cyclohexanone, acetone, and diethyl ketone oximes were analyzed using a Coleman Model 11 spectrophotometer at a wave-length of 425 mμ and using a concentration (3-fold excess) of 2,4-dinitrophenylhydrazine which did not saturate both the aqueous acid and carbon tetrachloride phases. Because of one or of both these factors, the calibration curve deviated slightly from a straight line.

The major absorption peak of 2,4-dinitrophenylhydrazones in chloroform has been stated to be in the region 366 to 368 mμ (15). The visible color band at 410 mμ was chosen for these analyses to avoid interferences from possible absorption by the rearrangement products, the amides. As a further check on possible interference from the amides, a sample of each oxime in sulfuric acid was subjected to rearrangement conditions for prolonged periods of time. Analysis of each mixture indicated complete rearrangement, *i.e.*, the concentration of the oxime was zero within the limits of error.

An approximation of the distribution of the 2,4-dinitrophenylhydrazone between the aqueous acid and the carbon tetrachloride layers was desired. A known quantity of 2,4-dinitrophenylhydrazone was dissolved in carbon tetrachloride which had been equilibrated with reagent and aqueous acid in the same manner as the oxime samples. The optical density

then was determined in the usual manner, and the calculated concentration was compared with the known concentration. The amount of 2,4-dinitrophenylhydrazone in the carbon tetrachloride layer was found to be as follows: cyclohexanone 99%; cyclopentanone 99%; diisobutyl ketone 95%; diisopropyl ketone 83%. The poor extraction of the diisopropyl ketone-2,4-DNPH by carbon tetrachloride would seem to make questionable the results obtained on the rates of rearrangement of this oxime. It is pointed out, however, that the calibration curve was constructed using conditions identical to the method of analysis of the oximes for the rate determinations, even to the extent of controlling the time and temperature of digestion. The 83% extraction of diisopropyl ketone-2,4-DNPH by carbon tetrachloride is a measure of the equilibrium between ketone and reagent rather than a measure of solubility of the hydrazone in carbon tetrachloride. Calibration curves were used for all rate studies.

IV *Rate determinations.* Approximately 0.002 mole of oxime was cautiously dissolved in 20 ml. of concentrated sulfuric acid (Merck, 94.5%) contained in a glass-stoppered, 125-ml. Erlenmeyer. The flask was stoppered and immersed in a constant temperature bath. At approximately equal time intervals extending from zero time to half-life, a 2-ml. aliquot was removed by means of a special pipette with large-mouth tip. The aliquot was poured into a previously tared, screw-cap bottle containing 23.0 ml. of water. The bottle was reweighed and 0.300 g. of 2,4-dinitrophenylhydrazine was added. The determination was then carried out exactly as described in the analytical procedure section, and the concentration of the oxime was obtained from the calibration curve. About eight aliquots were determined for each run. The slope of the straight line obtained from the plot of log concentration of oxime *versus* time in minutes was determined by the method of least squares (16) to give the experimental rate constant. The logs of the experimental rate constants were plotted *versus* reciprocal absolute temperatures, and the slope of the straight line determined by the method of least squares. This slope was used to redetermine the "true" rate constants recorded in Table I. Deviation of the experimental from the true rate constants are also recorded.

V *Large scale preparation of caprolactam.* The data from the rate determinations suggested conditions under which the rearrangement of cyclohexanone oxime could be carried out on larger scale and with greater efficiency than by the method reported in *Org. Syntheses* (9). The two methods which were developed take into consideration the well-known fact that both the activation energy and heat of reaction of this rearrangement are relatively large, so that it is necessary to supply heat initially and then to provide means for dissipating heat as the rearrangement proceeds. Also, the methods utilize the minimum amount of sulfuric acid which is a nuisance and an expense to neutralize. The minimum amount of sulfuric acid has been found to be slightly more than one equivalent of *available* acid. In other words, all of the oxime must probably be complexed as the oxonium salt in order to prevent self-condensation reactions, and apparently the hydrate of sulfuric acid is not sufficiently acidic to form the oxonium salt or to prevent condensation reactions. Thus, if one mole of sulfuric acid is used containing 0.1 mole of water, it is considered that 0.9 mole of sulfuric acid is available for oxonium salt formation.

The first method which follows has the advantages of better quality product and of simpler technique and the disadvantages of prolonged waiting periods and of need of temperature controls. Sulfuric acid (250 ml., 95%, 4.45 moles containing 1.3 moles of water, or 3.15 moles of available sulfuric acid) was placed in a 1-l. Erlenmeyer, protected from moisture and cooled in ice-water. Lesser amounts of sulfuric acid (170 ml., 2.13 moles of available acid) led to condensation products, as noted by darkening of the reaction mixture and by lowering of the yield of caprolactam (70% together with 20% undistillable residue). Ground or small-crystalled cyclohexanone oxime (226 g., 2.0 moles) was added in 20–30 g. portions to the cold sulfuric acid with vigorous swirling and cooling between addition periods. If the temperature of the sulfuric acid-oxime mixture went much above 60–70°, a violent and uncontrollable rearrangement reaction took place. If sulfuric acid was added to the oxime, a violent reaction also took place because the solid oxime dissipates the heat

of salt formation very poorly. Both precautions, however, were easily taken. After the addition of the oxime was completed, the oxonium salt-sulfuric acid mixture (in the Erlenmeyer stoppered and equipped with a thermometer) was placed in a constant temperature water-bath (not an oil-bath) maintained at 60° and allowed to undergo rearrangement for approximately 90 hours or until an aliquot did not give a 2,4-dinitrophenylhydrazone which was soluble in carbon tetrachloride. During this time, the internal temperature reached the maximum of 65° and gradually fell to 60° while the color of the reaction mixture became bright yellow. The reaction mixture was poured into a 3-necked, 1-l. flask, equipped with stirrer and dropping-funnel, and surrounded by an ice-bath. Concentrated ammonium hydroxide (610 ml., 9 moles) was added dropwise to the stirred solution until the mixture was neutral. The upper, oily layer of caprolactam was separated in a separatory-funnel. The aqueous layer, containing solid ammonium sulfate, was then filtered, and the ammonium sulfate washed with a mixture of 75 ml. of ether and 75 ml. of ethylene chloride. The same wash was used to extract the aqueous filtrate and then was added to the caprolactam. The caprolactam solution was superficially dried with sodium sulfate. Caprolactam holds water tenaciously and in contact with water is insoluble in solvents such as ether and toluene. The solution was concentrated first at atmospheric pressure and then by means of an aspirator; the residue was distilled at 2.5 mm. in a short-path apparatus; b.p. of caprolactam at 2.5 mm., 109–110°; 201 g., (89%), m.p. 67–69° (previous softening).

The second method has the advantage of short reaction period and the disadvantages of lower quality product and of the necessity for close watching during the progress of the reaction. The method simply dissipates the heat of reaction by vaporization of an inert solvent. Similar methods are recorded in the patent literature (17), but they do not seem to be as efficient as the following method: cyclohexanone oxime (226 g., 2.0 moles) was dissolved in 200 ml. of concentrated sulfuric acid as described in the first method. In the meantime, a mixture of 100 ml. of benzene and 50 ml. of chlorobenzene was brought to vigorous reflux in a 3-necked, 1-liter round-bottomed flask, equipped with stirrer and two condensers, and heated by means of a Glas-Col mantle. The internal temperature of the refluxing liquid was about 95°. Toluene can be used in place of the above mixture, but some sulfonation may occur. Conc'd sulfuric acid (50 ml.) then was added to the boiling liquid forming a second layer. Immediately after this addition, the oxime salt-sulfuric acid mixture was added dropwise through one condenser to the stirred, boiling liquid mixture. The voltage for the heating of the Glas-Col mantle was reduced to and maintained at 50 volts during the addition. The oxime salt-sulfuric acid mixture was added at a rate of 1.5–2 drops per second so that the liquid could be seen to reflux. If the reflux stopped, the addition of oxime was immediately stopped and the mixture brought to rapid reflux again by means of the Glas-Col. If too much oxime accumulated in the 3-necked flask, during the lag period enough heat of reaction was evolved to flood both condensers. The addition was completed in two hours. The mixture was heated at reflux for an additional hour. The organic liquid layer then was decanted, and the sulfuric acid-caprolactam layer of dark brown color was cooled and neutralized with ammonium hydroxide as described in the first method. The yield of ϵ-caprolactam was 199 g., 88%, b.p. 109–110° at 2.5 mm.; the distillate had a slight yellow discoloration; m.p. 67–69° (previous softening). The caprolactam can be recrystallized from ether (18), but the following method proved more satisfactory: 185 g. of ϵ-caprolactam was recrystallized from a mixture of 185 ml. of petroleum ether (b.p. 70°) and 30 ml. of *tert*-butyl alcohol and yielded 161 g. of colorless, small crystals, m.p. 70.5–71.5°. The crystals held *tert*-butyl alcohol tenaciously so that it was necessary to air-dry them for several days or to dry them under a vacuum.

VI *Investigation of other rearrangement products.* The rearrangement products of cyclopentanone oxime (19), of cycloheptanone oxime (14, 20), of acetone oxime (7), and of diisopropyl ketoxime (21) have been previously investigated. With the exception of the last compound, the above rearrangement products were not further investigated.

N-Isopropylisobutyramide. Diisopropyl ketoxime (43 g.) was carefully dissolved in 50 ml. of concentrated sulfuric acid. The mixture was allowed to stand at room temperature for four days and then was poured slowly into a slurry of ice and ammonium hydroxide.

The amide was filtered, washed, and air-dried; it was contaminated with some of the original oxime and weighed 28.6 g. (67%). An additional 8 g. (18%) of crude amide was obtained by ether extraction of the aqueous filtrate. The combined crops were recrystallized from a mixture of 50 ml. each of petroleum ether (b.p. 70°) and methylcyclohexane; 27.3 g., (63%), m.p. 105.5–106.5°; reported (21) m.p. 107°. More vigorous conditions or a larger excess of sulfuric acid should have been used in the rearrangement.

N-Isobutylisovaleramide. Diisobutyl ketoxime (29.5 g.) in 40 ml. of concentrated sulfuric acid, maintained at 52° for 40 hours, yielded 27% of crude oxime (b.p. 108–120° at 2 mm.) and 73% of the amide (b.p. 143–147° at 2 mm., m.p. 68–71°, previous softening). Two recrystallizations of the crude amide from petroleum ether (b.p. 70°) gave large, transparent plates, m.p. 72.5–73°, in poor yield. This amide will be investigated further since its characterization does not appear to have been reported in detail (22).

SUMMARY

A colorimetric analysis of oximes or of ketones, based on the solubility of the 2,4-dinitrophenylhydrazones in carbon tetrachloride, was developed and utilized in a study of the rates of rearrangement of several symmetrical aliphatic and alicyclic ketoximes. Comparison of rates is briefly made. Two laboratory-scale methods of synthesis of ε-caprolactam were developed.

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REFERENCES

(1) PEARSON AND BALL, *J. Org. Chem.*, **14**, 118 (1949).
(2) PEARSON, BAXTER, AND MARTIN, *J. Org. Chem.*, **17**, 1511 (1952).
(3) PEARSON AND BRUTON, *J. Org. Chem.*, **19**, 957 (1954).
(4) WICHTERLE AND ROCEK, *Collection Czechoslov. Chem. Communs.*, **16**, 591 (1951); *Chem. Listy*, **45**, 257 (1951).
(5) WICHTERLE AND ROCEK, *Chem. Listy*, **45**, 379 (1951).
(6) ROCEK AND BERGL, *Chem. Listy*, **47**, 472 (1953); *Collection Czechoslov. Communs.*, **16**, 599 (1951); **18**, 726 (1953).
(7) MCLAREN AND SCHACHAT, *J. Org. Chem.*, **14**, 254 (1949).
(8) HILDEBRAND AND BOGERT, *J. Am. Chem. Soc.*, **58**, 650 (1936).
(9) ECK AND MARVEL, *Org. Syntheses*, Coll. Vol. II, 77 and 371 (1943).
(10) BROWN, BREWSTER, AND SHECHTER, *J. Am. Chem. Soc.*, **76**, 467 (1954).
(11) MCELVAIN, *Characterization of Organic Compounds*, The MacMillan Co., New York, 1953.
(12) SHRINER AND FUSON, *Identification of Organic Compounds*, John Wiley and Sons, New York, 1948.
(13) TIMMERMANS, *Bull. soc. chim. Belg.*, **36**, 507 (1927).
(14) RUZICKA, KOBELT, HÄFLIGER, AND PRELOG, *Helv. Chim. Acta*, **32**, 544 (1949).
(15) JOHNSON, *J. Am. Chem. Soc.*, **75**, 2720 (1953); BRAUDE AND JONES, *J. Chem. Soc.*, 498 (1945); RAMIREZ AND KIRBY, *J. Am. Chem. Soc.*, **76**, 1037 (1954).
(16) MELLOR, *Higher Mathematics*, Dover Publications, New York, 1946, p. 326.
(17) U.S. Patent 2,573,374 [*Chem. Abstr.*, **46**, 7585 (1952)]; U.S. Patent 2,297,520 [*Chem. Abstr.*, **37**, 1451 (1943)]; British Patent 594,263 [*Chem. Abstr.*, **42**, 2268 (1948)].
(18) Japanese Patent 157,331 [*Chem. Abstr.*, **44**, 1531 (1950)].
(19) WALLACH, *Ann.*, **312**, 179 (1900).
(20) WALLACH, *Ann.*, **309**, 19 (1899); COFFMAN, COX, MARTIN, MOCHEL, AND VAN NATTA, *J. Polymer Sci.*, **3**, 85 (1948); BLICKE AND DOORENBOS, *J. Am. Chem. Soc.*, **76**, 2317 (1954).
(21) MEYER AND WARRINGTON, *Ber.*, **20**, 500 (1887).
(22) HARVILL, HERBST, SCHREINER, AND ROBERTS, *J. Org. Chem.*, **15**, 662 (1950).