

It was considered of interest to determine the extent of possible polymerization in gum rosin in the range of 275°C. (decarboxylation begins to become noticeable at 275°C.). Accordingly, a sample of commercial gum rosin was heated at 275°C. under nitrogen and sampled at intervals, and the nonvolatile portion was determined by a modification of the evaporative technique recently reported (Leonard *et al.*, 1965). Neutrals-free gum rosin gave somewhat the same results (see Figure 5).

Literature Cited

- Brooks, T. W., Fisher, G. S., Joye, N. M., Jr., *Anal. Chem.* **37**, 1063 (1965).
Fleck, E. E., Palkin, S., *Ind. Eng. Chem., Anal. Ed.* **14**, 146 (1942).
Joye, N. M., Jr., Lawrence, R. V., *J. Chem. Eng. Data* **12**, 279 (1967a).
Joye, N. M., Jr., Lawrence, R. V., unpublished results, 1967b.

- Leonard, R. H., Kubitz, K. A., Rockwell, J. M., *J. Am. Oil Chemists' Soc.* **42**, 111 (1965).
Lewis, J. B., Hedrick, G. W., unpublished results, 1966.
Lloyd, W. D., Hedrick, G. W., *J. Org. Chem.* **26**, 2029 (1961).
Stinson, J. S., Lawrence, R. V., *Ind. Eng. Chem.* **46**, 784 (1954).
Takeda, H., Schuller, W. H., Lawrence, R. V., *J. Org. Chem.* **33**, 1683 (1968).

RECEIVED for review May 1, 1968
ACCEPTED June 24, 1968

One of the laboratories of the Southern Utilization Research and Development Division. Agricultural Research Service, U.S. Department of Agriculture.

Hiroshi Takeda and Hideo Kanno were National Academy of Sciences-National Research Council Postdoctoral Research Fellows.

A LOW TEMPERATURE BECKMANN REARRANGEMENT WITH SO₃ INCLUDING SEPARATION OF CAPRIMIDYL SULFATE AS A NEW COMPOSITION

A. F. TURBAK¹

Esso Research and Engineering Co., Linden, N. J.

Cyclohexanone oxime can be rapidly and safely converted to caprolactam at low temperatures by use of complexed SO₃. All complexing agents do not work. Under these mild conditions, it is possible to use only equimolar amounts of SO₃ and thereby to isolate the previously hypothetical "caprimidyl sulfate" intermediate as a new composition of matter. Reaction conditions leading to best lactam yields are presented. Aromatic oximes can also be rearranged by use of triethyl phosphate complexing, which deactivates the SO₃ sufficiently so that it does not react with the aromatic ring. Aldoximes undergo dehydration rather than rearrangement.

THE REACTION of SO₃ with oximes, particularly cyclohexanone oxime, is very vigorous and potentially explosive. To moderate the reactions it is usually necessary to use large amounts of concentrated sulfuric acid as a solvent and heat absorber. For example, the "Organic Syntheses" (Blatt, 1950) procedure for rearranging 100 grams of cyclohexanone oxime to caprolactam recommends dividing the 100 grams into 10 samples of 10 grams each in order to control the ensuing vigorous reaction in sulfuric acid. The large amount of sulfuric acid usually employed for the production of caprolactam from cyclohexanone oxime leads to formation of a considerable excess of by-product sulfate. Since a commercial producer of caprolactam usually manufactures 5 pounds of sulfate for each pound of caprolactam, he is really in the sulfate business and isolates caprolactam as a valuable by-product.

By using equimolar amounts of complexed SO₃ cyclohexanone oxime can be rearranged smoothly and rapidly

to caprolactam at temperatures below 50°C. This procedure offers the advantages of safety, control, and drastically reduced sulfate salt formation. This mild procedure also allows us to separate the heretofore hypothetically proposed caprimidyl sulfate intermediate as a new solid composition.

Discussion

This report discusses the various complexing agents for SO₃ useful in the rearrangement, and describes the effect of reaction conditions on caprolactam yield. Further, it presents procedures for the separation and purification of the caprimidyl sulfate intermediate. Finally, it presents some results on the use of complexed SO₃ with other ketoximes and aldoximes.

Complexing Agents Employed. The use of various reagents, including SO₃ solutions in fuming sulfuric acid, for catalyzing the Beckmann rearrangement has been

¹ Present address, Tee-Pak, Inc., Danville, Ill.

reviewed in "Organic Reactions" (Donaruma and Heldt, 1960). This comprehensive review does not mention the use of complexed SO_3 . The use of complexing agents to reduce the extreme reactivity of SO_3 and the various reactions of these complexed species has recently been reviewed by Gilbert (1966). Recently, the author reported the use of phosphates as versatile complexing species in controlling SO_3 activity (Turbak, 1962; Turbak and Livingston, 1963). In this study, triethyl phosphate, dioxane, dimethylformamide, and pyridine were investigated as possible complexing agents (Table I).

These data definitely indicate that all complexing agents are not useful for rearranging oximes to lactams. The fact that triethyl phosphate- SO_3 complexes give homogeneous solution in the dichloroethane employed as solvent cannot be a controlling factor since dioxane, which gives a heterogeneous solid mixture in dichloroethane, also performs well. The tar formation might well be the result of further reaction of DMF and pyridine with the intermediate caprimidyl sulfate. However, no data are available to substantiate this view.

Reaction Variables Defined. As originally run, the complexing agent was dissolved in dichloroethane and an equimolar amount of SO_3 was added slowly at 0° to 5°C . The complex was then brought to 25°C ., and an equimolar amount of cyclohexanone oxime (dissolved in dichloroethane) was added over a 10-minute period at a temperature of $27^\circ \pm 2^\circ\text{C}$. with external cooling. After addition was complete, the temperature was allowed to rise spontaneously to a maximum of about 46° to 50°C . over a 20 to 30-minute period. The caprimidyl sulfate was then isolated by precipitation with petroleum ether, and neutralized to give the caprolactam.

Using this general procedure, the effects of addition sequence, addition temperature, and oxime dryness on subsequent caprolactam yields were investigated.

EFFECT OF ADDITION SEQUENCE. In the regular procedure, the cyclohexanone oxime was added to the complexed SO_3 . In subsequent runs, simultaneous addition of oxime and phosphate complexed SO_3 and inverse addition of complexed SO_3 to the oxime were tried (Table II). Obviously addition of oxime to the complexed SO_3 is the preferable method of reaction.

Table I. Effect of Complexing Agents

Complexing Agent	Yield of Lactam, %
Triethyl phosphate	82
Dioxane	80
Dimethylformamide	Tar
Pyridine @ 25°C .	Tar
Pyridine @ 60°C .	Tar

Table II. Effect of Addition Sequence

Addition	Lactam Yield, %
Regular (oxime added to complexed SO_3)	82
Simultaneous	65
Inverse	0

^a No spontaneous exotherm until solid is filtered, then violent decomposition.

Special note: A word of caution regarding the inverse addition procedure (when complexed SO_3 is added to the oxime) is necessary. The reaction appears to be dormant, and the solid which can be separated by petroleum ether precipitation is stable until the solvent is removed in the dry box, at which point it decomposes violently. This procedure was not further investigated.

EFFECT OF ADDITION TEMPERATURE. When the cyclohexanone oxime is added to the complexed SO_3 , there is some heat evolution, and the oxime must be added rather slowly or the reaction must be cooled. The maximum exothermic temperature reached is a function of the original addition temperature (Table III). Thus, overall yield is fairly constant as long as the addition temperature is kept below about 35°C .

EFFECT OF OXIME DRYNESS. Cyclohexanone oxime has some moisture as normally supplied. Experiments showed that drying the oxime by azeotroping in a dichloroethane solution or by melting under vacuum resulted in a 12% and 8% respective increase in lactam yields.

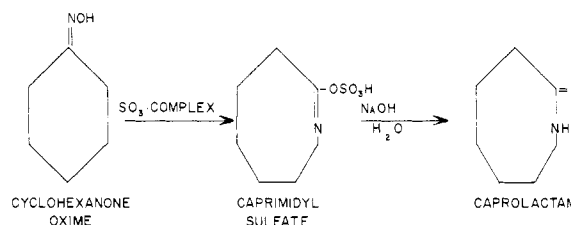
Use of Other Oximes. To determine the effect of oxime structure, reactions were run using phosphate complexed SO_3 , an acetophenone oxime, and a benzaldoxime. Since the 1-to-1 complex of SO_3 with trialkyl phosphate does not react with benzene rings, it is possible to use aromatic oximes without simultaneous ring sulfonation.

Acetophenone oxime yielded acetanilide. Benzaldoxime, however, underwent dehydration to benzonitrile. This reaction of aldoximes is common. It is somewhat surprising, however, that benzonitrile rather than formamide would be produced under such mild conditions.

Experimental

Because only equimolar amounts of SO_3 and oxime are employed in this procedure and because of the mild conditions it is possible to isolate the heretofore hypothetical caprimidyl sulfate as a new composition of matter.

The reaction proceeds according to the equation:



Preparation of Caprimidyl Sulfate. To 100 cc. of dichloroethane add 17.6 grams (0.2 mole) of dioxane and then add 8.4 cc. (0.2 mole) of SO_3 dropwise with stirring, while maintaining the temperature at 5° to 10°C . with external cooling. The SO_3 -dioxane complex separates from solution as a white solid.

Bring this liquor to 25°C . and add 22.6 grams of cyclohexanone oxime dissolved in 50 cc. of dichloroethane as a slow stream, while maintaining the reaction at $25^\circ \pm 2^\circ\text{C}$. After addition, allow the temperature to rise to 48°C . spontaneously, during which the milky liquor turns to a clear light-yellow solution.

Table III. Effect of Reaction Temperature

Addition Temp., $^\circ\text{C}$.	Max. Exothermic Temp., $^\circ\text{C}$.	Lactam Yield, %
25	40	80
5	61	77
5	30 (Controlled)	70
35	35	77
60	84	5

When the reaction again drops to 25° C., add the reaction liquor to 400 cc. of vigorously stirred petroleum ether. A heavy oil separates, which on further stirring hardens to a light cream-colored solid. Filter this solid in a dry box through a filtered glass funnel, to recover 42.7 grams of product.

This product is further purified by redissolution in fresh dichloroethane and reprecipitation with fresh petroleum ether. The purified material is dried in the dry box and is extremely hygroscopic. In fact, if a very well dried stream of nitrogen is not employed in the dry box, it turns into a puddle in a matter of hours. The product was analyzed for C, H, and S and checked almost exactly for caprimidyl sulfate. This solid has a melting point of 122° C. as compared with 88° C. for cyclohexanone oxime, and 67° C. for caprolactam. It can be converted quantitatively to caprolactam by treatment with sodium hydroxide. To demonstrate that this solid was not caprolactam sulfate, the sulfate was prepared from known caprolactam. The physical properties and behavior of the two products were entirely different.

If desired, 36.6 grams of triethyl phosphate (0.2 mole) can be used in place of the 17.6 grams of dioxane. This gives a liquid rather than a solid complex specie.

Conclusions

Caprolactam can now be prepared in good yields under mild and safe conditions at low temperatures by use of phosphate or dioxane complexed SO₃. Caprimidyl sulfate

has been isolated as a new composition of matter. It is a very hygroscopic but stable white solid, melting at 122° C. Other ketoximes can be used but aldoximes undergo dehydration rather than rearrangement. Aromatic ketoximes can be rearranged by phosphate complexed SO₃ without ring sulfonation.

Literature Cited

- Blatt, A. H., Ed., "Organic Syntheses," Coll. Vol. 2, p. 77, Wiley, New York, 1950.
Donaruma, L. G., Heldt, W. Z., "Organic Reactions," Vol. 11, pp. 1-156, Wiley, New York, 1960.
Gilbert, E. E., "Sulfonation and Related Reactions," Wiley, New York, 1966.
Turbak, A. F., *IND. ENG. CHEM. PROD. RES. DEVELOP.* 1, 275 (1962).
Turbak, A. F., Livingston, J. R., Jr., *IND. ENG. CHEM. PROD. RES. DEVELOP.* 2, 229 (1963).

RECEIVED for review August 7, 1967

ACCEPTED May 13, 1968

Division of Organic Chemistry, 153rd Meeting, ACS, Miami, Fla., April 1967.

RAPID AND COMPREHENSIVE CRUDE OIL EVALUATION WITHOUT DISTILLATION

V. FRANCES GAYLOR AND CAROLINE N. JONES

The Standard Oil Company (Ohio), 4440 Warrensville Center Rd., Cleveland, Ohio 44128

A rapid method for evaluating chemical and physical properties of crude oil has been developed. Yield and quality of all fractions through asphalt are obtained in two to three hours. The results provide much, and often sufficient, information to judge the refining value of a crude; and analysis time and costs are considerably less than required for a conventional distillation assay of comparable scope. The method consists of six tests made on whole crude oil. The tests are gravity, per cent sulfur, nitrogen, pentane insolubles, polarographically measured condensed aromatics, and gas chromatography. Composition parameters obtained by applying these tests to 23 crude oils were correlated with quality tests of the 10 fractions per crude obtained from an 8-gallon batch still. Correlations ranged from acceptable to excellent and included such important quality parameters as gravity of all fractions, smoke point and freezing point of kerosine, wax content and viscosity index of lubricating oils, U.O.P. "K" factor and carbon residue of cracking stocks, and retained ductility and petroline VGC of asphalt.

A COMPLETE crude oil assay should define both quantity and quality of all major fractions contributing to value of this raw material. Quantity of each fraction is conventionally determined by distillation of a sample of the crude. Quality is then determined by separate testing of each major fraction recovered. Time and costs thus multiply in direct proportion to the number of fractions examined during any type of distillation assay.

Significant reductions in time and costs of evaluating crude oils probably can be achieved only by eliminating

the distillation step. Analytical tests applicable to whole crude oil, but which will adequately characterize all distillation fractions of the crude, are then needed. The present work used six such tests (Table I). Quantity and quality of all crude oil fractions, through asphalt, are calculated from information derived from these simple tests. The gas chromatographic analysis provides experimental boiling range distribution data up to 725° F. Yields of higher boiling fractions are predictable from knowledge of quantity of 700° F.+ bottoms, combined with