A typical duplicate run yielded 52.5% of VII, b.p. 94–97° (0.10 mm.), $n^{26}D$ 1.4853.

E. **Proof of Structure for the Cyclic Formal of *cis*-3,4-Dihydroxycyclohexylmethanol (IV).** 1. **Methylation of 5-Hydroxymethylhexahydrobenzo-*cis*-1,3-dioxole (VII).**—In a microreaction flask was heated 0.6 g. (0.026 g.-atom) of sodium metal in 30 ml. of toluene. To the sodium at reflux was added dropwise over 45 min. a solution of 4.00 g. (0.0254 mole) of VII in 20 ml. of toluene (N_2 atmosphere). The formation of the alkoxide was allowed to proceed overnight. After 14 hr., dimethyl sulfate, 3.2 g. (0.025 mole) in 10 ml. of toluene, was added over 15 min. and the reaction mixture allowed to reflux 2 hr. Methanol, 10 ml., was added and the resulting toluene solution washed with dilute ammonia water and dried over anhydrous sodium sulfate. After removal of the solvent the residue was distilled. One main fraction was collected, 3.0 g. (73% yield), of 5-methoxymethylhexahydrobenzo-*cis*-1,3-dioxole, b.p. 58° (0.1 mm.), $n^{27}D$ 1.4605.

Anal. Calcd. for $C_9H_{16}O_3$: C, 62.76; H, 9.34. Found: C, 62.45; H, 9.37.

2. **Hydrolysis of the Methylated Formal of IV and Determination of 1,2-Glycol Content.**—A 0.2811-g. sample of the methylated formal of IV, 50 ml. of water, and 5 drops of concentrated HCl were heated on a steam bath overnight. The resultant homogeneous solution was diluted quantitatively to 100 ml. and the concentration of 1,2-glycol structure determined by periodic acid titration.[7] Aliquots of the hydrolyzed glycol took up 98–110% of the theoretical amount of periodic acid after a 1-hr. reaction time at 25°.

Acknowledgment.—The *trans*-hexahydrobenzo-1,3-dioxole was synthesized for the first time by Dr. Newman M. Bortnick of the Rohm and Haas Company.

[7] R. A. B. Bannard and L. R. Hawkins, *Can. J. Chem.*, **36**, 1254 (1958).

Synthesis and Polymerization of Propanesultam

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Propanesultam has been prepared by addition of thiolacetic acid to allyl chloride, oxidation of the adduct with aqueous chlorine to 3-chloropropanesulfonyl chloride, reaction with ammonia, and cyclization of the resulting 3-chloropropanesulfonamide in alcoholic base. Chromatographically pure propanesultam had m.p. 23.1–23.2°, b.p. 156–157 (2 mm.), $n^{22}D$ 1.4826; the N-benzoyl derivative melted at 171–172°. Polymerization of propanesultam of 99.1% purity has been investigated using a variety of catalysts. Basic catalysts such as sodium hydride, sodium and potassium hydroxides, potassium phenoxide, or tetramethylguanidine are effective in producing polymer of high molecular weight, m.p. 257–260°, $[\eta]$ 0.77 dl./g., particularly when used with an N-alkane- or N-arenesulfonyl-1,3-propanesultam as cocatalyst, as for example, N-(*p*-toluenesulfonyl)-1,3-propanesultam. Lewis acids were ineffective under a variety of conditions. Octadecylamine hydrochloride, aniline hydrochloride, picric acid, *p*-toluenesulfonic acid, mesitylenesulfonic acid, and benzenesulfonyl chloride effected polymerization, but only polymer of low molecular weight was produced.

Recently, the results of a study by Libby[1] of the polymerization of propanesultam have appeared. At the time, we were investigating the same reaction and both our studies and Libby's have shown that propanesultam polymerizes readily in the presence of a strong base as a catalyst and an N-acylpropanesultam as an initiator by a mechanism analogous to that proposed for the base-catalyzed polymerization of 2-pyrrolidinone.[2,3]

Our work on base-catalyzed sultam polymerization has confirmed the results reported by Libby. We have in addition investigated the previously unknown and much less facile polymerization of propanesultam in the presence of acid catalysts.

Best results have been obtained with sodium hydride as the basic catalyst in conjunction with N-benzenesulfonyl-1,3-propanesultam, but other strong bases may be used (Table I). Sodium hydroxide and potassium hydroxide are only slightly less effective, and potassium phenoxide is also quite effective. The alkali metal salts of 1,3-propanesultam itself may be used as catalysts in the polymerization. In general, amines do not give good results, but tetramethylguanidine did.

It has been found that sodium hydride and other basic catalysts should be used in concentrations of 0.3–1.0 mole % based on monomer. An excess of catalyst over initiator is needed to prevent chain transfer reactions which result in products of low molecular weight. Usually about two moles of base have been employed per mole of initiator, and best results have been obtained when the initiator was used in a concentration of 0.25–0.50 mole % based on the amount of monomer used.

Wide variation in the structure of the initiator is permissible. In general, any N-alkane- or N-arenesulfonyl-1,3-propanesultam is effective, as, *e.g.*, N-(*p*-toluenesulfonyl)-1,3-propanesultam, N-(2,5-dimethylbenzenesulfonyl)-1,3-propanesultam, N-(1-naphthalene sulfonyl)-1,3-propanesultam, or N-(2-naphthalenesulfonyl)-1,3-propanesultam. It also is possible to employ an alkane- or arenesulfonyl halide in conjunction with a strong base, in which case the active N-alkane-

TABLE I

POLYMERIZATION OF 1,3-PROPANESULTAM

Catalyst	Weight %	Temp., °C.	Time, hr.	% conversion	M.p. of polymer, °C.
NaH[a]	0.3	130	18	64.4	257-260
NaOH[a]	0.5	120	5	23.4	243-250
KOH[a]	0.7	130	3.5	35.8	240-244
C_6H_5OK[a]	0.3	127	5	29.1	238-246
$(Me_2N)_2C:NH$[a]	0.3	110	4.5	33.8	236-242
Octadecylamine hydrochloride	0.5	164	22	4.5	252-255
Octadecylamine hydrochloride	1.5	190	18	22.9	250-257
Aniline hydrochloride	0.4	165	22	1.5	228-232
Aniline hydrochloride	0.4	190	21	14.6	250-253
Picric acid	0.5	160	18	Trace	
Picric acid	0.5	190	20	13.0	230-242
p-Toluenesulfonic acid	0.7	130	20	Trace	
p-Toluenesulfonic acid	0.7	160	22	7.1	238-242
Mesitylenesulfonic acid	0.7	130	22	Trace	
Mesitylenesulfonic acid	0.7	160	22	10.8	232-236
Benzenesulfonyl chloride	0.7	160	18	9.5	223-228

[a] N-Benzenesulfonyl-1,3-propanesultam was added as an initiator.

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[1] W. H. Libby, U. S. Patent 2,983,713 (May 9, 1961).

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

[3] G. Champetier and H. Sekiguchi, *Compt. rend.*, **249**, 108 (1959).

or N-arenesulfonyl-1,3-propanesultam is formed *in situ.* It also has been found possible to employ N-acyl-1,3-propanesultam derivatives, such as N-benzoyl-1,3-propanesultam as initiators. Results when using the acyl derivatives were considerably better than those obtained without any initiator, but these compounds were not so effective as the N-alkane- or N-arenesulfonyl compounds.

None of the conditions tried in the study of the acid-catalyzed polymerization of propanesultam gave polymer of high molecular weight. Even the conversion to polymer in these reactions did not exceed 30%, except where conditions favored chain transfer, and polymer of exceedingly low molecular weight was formed. The maximum melting point and intrinsic viscosity of these polymers were approximately 250° and 0.10 dl./g., respectively, while base-catalyzed polymerization of the sultam routinely produced polymers melting at 260–265° with viscosities of 0.8 dl./g. or higher. Except for differences attributable to low molecular weight, the acid-produced polymers resembled those formed in base-catalyzed reactions. The polymers dissolved readily in aqueous alkali and in concentrated sulfuric acid, were sparingly soluble in dimethyl sulfoxide and N,N-dimethylformamide, and insoluble in most other organic solvents, including propanesultam. The major difference, other than small shifts in a few of the bands, between the infrared spectrum of polypropanesultam and that of the monomer, was that the former lacked a medium-intensity band at 10.0 μ, which was tentatively ascribed to a ring absorption of the monomer.

The polymerizations were all run in bulk at temperatures ranging from 130 to 210° with a variety of Lewis and protonic acid catalysts. No polymer was obtained using manganese(III) oxide, antimony(III) oxide, aluminum chloride, titanium(IV) chloride, or boron fluoride etherate at concentrations of 0.5 or 1.0% by weight of monomer, at 130–160° for 3 to 10 hr. None of the catalysts was appreciably soluble except boron fluoride etherate. The investigation was not extended to higher temperatures since the preliminary experiments had indicated that the catalytic activity of the Lewis acids would be feeble. Boron fluoride etherate, in the presence of traces of water, opened the sultam ring giving small amounts of the corresponding sultaine, $^{+}NH_3(CH_2)_3SO_3^{-}$, m.p. 198–200° dec. (reported m.p. 200° dec.[4]), but produced no polymer.

All of the protonic acids investigated had some catalytic activity, but the sulfonic acids appeared to be the most effective as judged by the temperature at which polymer formation became detectable (Table I). Even with the sulfonic acids, however, the polymerization was quite slow and the conversion was small. The rate of polymerization increased with increasing temperature. Decomposition of the mixture occurred at a temperature which varied with the nature and concentration of the catalyst, but was generally only about 40–50° higher than that at which polymerization became detectable.

Neither the pure monomer nor the washed and dried polymer decomposed at temperatures up to 250°. Yet polymers which had been partly degraded during preparation underwent extensive decomposition at 250°. It also was found that the addition of minute amounts of either basic or acidic catalysts to colorless melts of polypropanesultam at about 260° caused rapid darkening and a copious evolution of reduced-sulfur compounds. With both acidic and basic materials, the most active polymerization catalysts were also most effective in initiating decomposition, although polymerization always occurred at the lower temperature. Traces of water in acid-catalyzed polymerization mixtures also increased the rate of decomposition, probably because of hydrolysis, which increased the effective concentration of acid.

In order to obtain polymer of high molecular weight in the experiments with basic catalysts, it was necessary to employ highly purified monomer. Distillation of the sultam under reduced pressure gave material of 99.1% purity as determined by vapor phase chromatographic analysis. Further purification was effected by fractional melting,[5,6] or more conveniently, by low temperature recrystallization from ether–alcohol mixtures. Both techniques gave material which showed no impurities in the vapor phase chromatograph. This additional purification of the monomer did not produce any improvement in either the conversion or the molecular weight of the product in the acid-catalyzed polymerizations and the vacuum-distilled sultamwas used directly in most of the experiments.

Experimental

Melting points were taken on a Fisher-Johns block and are uncorrected. Viscosities were determined rapidly in concentrated sulfuric acid. Polypropanesultam slowly degrades in this solvent, as evidenced by a decline in viscosity, and the reported values were corrected for this effect by plotting a viscosity–time curve and extrapolating to zero time.

Infrared spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer. Propanesultam was analyzed on a 7-ft. glass-bead column with Apiezon as a substrate with a programmed temperature from 100° to 225°, using an F & M Model 202 chromatograph.

Preparation of Propanesultam.—Propanesultam has been prepared by pyrolysis of 3-hydroxy-[7-9] or halogen-substituted[4] propanesulfonamides, by treatment of 3-chloropropanesulfonamide with base[1] and by pyrolysis or treatment of 3-aminopropanesulfonyl chloride hydrochloride with base.[10]

We have found 3-chloropropyl thiolacetate to be a convenient starting material for large-scale laboratory preparations of propanesultam. The thiol ester can be synthesized easily by the peroxide-catalyzed addition of thiolacetic acid to allyl chloride,[11] and is smoothly oxidized to 3-chloropropanesulfonyl chloride by the action of aqueous chlorine. Treatment of the sulfonyl chloride with ammonia and cyclization of the resulting 3-chloropropanesulfonamide in ethanolic potassium hydroxide affords the sultam in good over-all yield.

Thiolacetic acid was prepared by the method of Ellingboe[12] in 85% yield, b.p. 87–90°.

3-Chloropropyl thiolacetate, b.p. 74–76° (6 mm.), was prepared successfully several times from thiolacetic acid and allyl chloride by the method of Sjoberg.[11] When carefully purified thiolacetic

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(4) W. F. Erman and H. C. Kretschmar, *J. Org. Chem.*, **26**, 4841 (1961).

(5) A. R. Glasgow and G. Ross, "Apparatus for Purification of Materials by Fractional Melting," National Bureau of Standards Report 2145.

(6) J. G. Aston and S. Mastrangelo, *Anal. Chem.*, **22**, 636 (1950).

(7) F. Asinger and F. Ebeneder, *Ber.*, **75B**, 344 (1942); German Patent 740,814 (September 9, 1943); *Chem. Abstr.*, **40**, 611 (1946).

(8) Ruhrchemie, A-G., British Patent 752,227 (July 4, 1956); *Chem. Abstr.*, **51**, 4415 (1957).

(9) I. G. Farbenind., A-G., Belgian Patent 450,737 (June, 1943); *Chem. Abstr.*, **42**, 209 (1948).

(10) H. Feichtinger and H. Tummes, German Patent 930,210 (July 11, 1955); *Chem. Abstr.*, **50**, 8748 (1956). U. S. Patent 2,749,340 (June 5, 1956); *Chem. Abstr.*, **50**, 11361 (1956). U. S. Patent 2,866,786 (December 30, 1958); *Chem. Abstr.*, **53**, 6087 (1959).

(11) B. Sjoberg, *Ber.*, **74B**, 64 (1941).

(12) E. K. Ellingboe, *Org. Syn.*, **31**, 105 (1951).

acid was used, however, the reaction proceeded with great violence, and it was necessary to cool the mixture and add the acid gradually to the allyl chloride.

3-Chloropropanesulfonyl chloride was prepared by modification of the method of Rumpf.[13] To 596 g. (3.90 moles) of 3-chloropropyl thiolacetate in a 5-l., three-necked flask was added 1 l. of water and about 500 g. of crushed ice. The flask was immersed in an ice bath, and its contents were vigorously stirred while gaseous chlorine was passed in at a rapid rate. Crushed ice was added to maintain the temperature at 5–10°. The initially colorless, turbid mixture quickly acquired a bright yellow color, which slowly changed to pink, then to orange. The orange color persisted for about 1 hr., then faded to give a colorless, turbid mixture. After a short time, a persistent color of chlorine appeared in the liquid, and the reaction was stopped. The aqueous solution was decanted from a heavy colorless oil, washed twice with ether, and discarded. The combined oil and ether extracts were washed with water and dried over anhydrous sodium sulfate. Filtration and distillation of the ether gave a slightly yellow oil, which was distilled at reduced pressure. The distillate, a clear, colorless liquid, weighed 590 g. (87%) and boiled at 107–108° at 6 mm.

3-Chloropropanesulfonamide.—A 3-l. flask containing 138 ml. (approximately 2.2 moles) of concentrated aqueous ammonia and 1 l. of ether was cooled in an ice bath. A solution of 177.5 g. (1.00 mole) of 3-chloropropanesulfonyl chloride in 500 ml. of ether was added to the stirred mixture at such a rate as to maintain the temperature at 5°. After further stirring at ice temperature for 30 min., the ether layer was separated and dried over anhydrous sodium sulfate. The ether solution, filtered, treated with petroleum ether (b.p. 30–60°) to faint turbidity, and cooled in a freezer, deposited 56.5 g. of white needles melting at 64.0–64.5°, lit.[14] m.p. 63°). The filtrate was evaporated to dryness under reduced pressure, giving a sticky, white solid residue which was combined with the solid obtained by evaporation of the aqueous layer of the reaction mixture and extracted three times with 500-ml. portions of hot benzene. The benzene extracts gave, upon cooling, an additional 48.5 g. of white needles melting at 64.0–64.5°. The total yield of pure material was 130 g. (87%). The 55 g. of material insoluble in benzene was mostly ammonium chloride. Evaporation of the benzene extracts gave 25 g. of a yellow oil which distilled at 138–140° at 5 mm. The colorless distillate was insoluble in acid and base and contained sulfur, but no nitrogen or chlorine. It was not investigated further.

Propanesultam.—To a solution of 115 g. (0.73 mole) of 3-chloropropanesulfonamide in 1 l. of absolute ethanol, which had been freshly distilled over potassium hydroxide, was added a solution of 40.9 g. (0.73 mole) of potassium hydroxide in 200 ml. of absolute ethanol. The solution became turbid almost at once. After refluxing for 45 min., a copious white precipitate had formed, and the solution was neutral. A solution of 2.0 g. of potassium hydroxide in ethanol was added, and the mixture was refluxed for 30 min. At the end of that time, the mixture, still strongly basic, was cooled and filtered. After having been washed with two 25-ml. portions of ethanol and dried, the salt residue weighed 54 g. (99%). The combined filtrate and washings were carefully neutralized with concentrated hydrochloric acid and again filtered. Removal of the alcohol from the filtrate at reduced pressure gave 89.5 g. of a slightly yellow oil contaminated with a small amount of potassium chloride. Distillation of the oil at reduced pressure gave 3.5 g. of a volatile, yellow liquid with a vile mercaptan odor, 74 g. of an odorless yellow liquid boiling at 156–157° (2 mm.), and 9.0 g. of viscous black residue. The main fractions solidified, melting at 23.0-23.1°. The product on redistillation boiled unchanged, giving 70 g. of very slightly yellow material melting at 23.1–23.2° (residue 2.5 g. of black viscous oil). Treatment of the product with decolorizing carbon gave 67 g. (76%) of colorless propanesultam, b.p. 156–157° (2 mm.), $n^{25}\text{D}$ 1.4826; lit.[6] b.p. 180° (5 mm.); lit.[7] 180° (1 mm.), $n^{25}\text{D}$ 1.4815. Vapor phase chromatographic analysis of the product showed three low-boiling impurities totaling 0.9%. The major infrared absorptions (in μ) of the product were at 3.08 (vs), 3.40 (m), 7.20 (s), 7.60 (vs), 8.50 (vs), 8.80 (vs), 9.60 (m), 10.02 (m), 10.80 (m), and 13.7 (m). Weak absorptions occurred at 3.48, 6.88, and 11.35 μ.

Anal. Calcd. for $C_3H_7NO_2S$: S, 26.46. Found: S, 26.13.

N-Benzoylpropanesultam.—To 3.0 g. of propanesultam in 25 ml. of pyridine was added 3.5 g. of benzoyl chloride. The solution was refluxed for 2 hr., then cooled, and poured into water. A brown solid that formed was recrystallized thrice from ethanol, giving 4.5 g. of white plates melting at 171–172°.

Anal. Calcd. for $C_{10}H_{11}NO_3S$: C, 53.31; H, 4.92; N, 6.22; S, 14.24. Found: C, 52.21, 52.24, 51.93; H, 4.68, 4.82; N, 6.22; S, 14.1.

N-Methylpropanesultam.—To 16.3 g. (0.13 mole) of propanesultam was added 16.8 g. (0.13 mole) of dimethyl sulfate, and to this mixture, in small portions, a solution of 18 g. of potassium hydroxide in 75 ml. of water (required 1 hr.). The solution was filtered and evaporated to dryness at reduced pressure, leaving a yellow solid, which was extracted with four 100-ml. portions of ether. The combined ether extracts were treated with petroleum ether to turbidity and cooled, giving 8.5 g. of white crystalline material melting at 46.5–47.0°, lit.[6] m.p. 45–47°. The mother liquors gave an additional 2.0 g. of the same substance. Two recrystallizations from mixed ether and petroleum ether did not change the melting point.

Anal. Calcd. for $C_4H_9NO_2S$: C, 35.54; H, 6.71. Found: C, 35.18; H, 6.59.

N-Benzenesulfonylpropanesultam.—To 16 ml. of pyridine were added 5.0 g. (0.040 mole) of propanesultam and 5.2 ml. (7.2 g., 0.040 mole) of benzenesulfonyl chloride. The mixture became slightly warm and slowly turned deep red. After standing for 72 hr. at room temperature, the mixture was poured into 250 ml. of ice–water. The tan precipitate which formed was filtered, washed with water, and recrystallized from ethanol giving shiny yellow plates melting at 168–169°. Treatment of an acetone solution of the product with decolorizing carbon and a second recrystallization from ethanol gave 1.5 g. of white plates melting at 169.5–170.0°.

Anal. Calcd. for $C_9H_{11}NO_4S_2$: C, 41.36; H, 4.24. Found: C, 41.61, 41.64; H, 4.09.

N-*p*-Toluenesulfonylpropanesultam. A.—A 125-ml. erlenmeyer flask was charged with 0.5 g. of propanesultam and 20 ml. of water. To the solution was added 0.13 g. of sodium hydroxide and, after the base had dissolved, 0.76 g. of *p*-toluenesulfonyl chloride. The flask was warmed to 60° with vigorous stirring, the large crystals of *p*-toluenesulfonyl chloride slowly dissolved, and a fine white precipitate appeared. After 2 hr., the odor of *p*-toluenesulfonyl chloride could no longer be detected. The crystalline solid was washed with water, dried, and recrystallized twice from absolute ethanol, giving 0.82 g. (73%) of gleaming white plates melting at 205–206°.

Anal. Calcd. for $C_{10}H_{13}NO_4S_2$: C, 43.62; H, 4.83; N, 5.09; S, 23.29. Found: C, 42.99; H, 4.85; N, 4.99, 5.22; S, 21.35, 21.44.

B.—A small quantity of *p*-toluenesulfonic acid (Matheson) was held 4 hr. in a vacuum desiccator at 55° over phosphoric anhydride. To 0.0068 g. of this dried material in a small test tube was added 0.9507 g. of propanesultam which had been dried for 2 hr. at 157° in a stream of dry nitrogen. The mixture was allowed to react, under dry nitrogen, at 157 ± 1° for 22 hr. At the end of that time, the mixture was slightly yellow, but clear and fluid at the reaction temperature. Upon cooling to room temperature, a white solid separated, and the mixture became somewhat viscous. The material was treated with 20 ml. of cold water, producing a fine, white suspension, which was filtered, washed with 5 ml. of water, 15 ml. of acetone, and dried. The product weighed 0.0696 g. and melted at 228–232° to a very viscous, slightly yellow liquid. The conversion to polymer was 7.1% on a weight basis.

The combined aqueous acetone filtrates were evaporated to about 20 ml. on the steam bath. A small amount of a yellow, crystalline substance appeared at this point. The mixture was cooled and filtered, giving, after drying, 0.0051 g. of a crystalline material melting at 204–205°, which was identified as N-*p*-toluenesulfonylpropanesultam by comparison of infrared spectra and mixture melting point with an authentic sample (m.p. 205–206°). The yield, based on *p*-toluenesulfonic acid, was 45%.

Evaporation of the aqueous filtrate to dryness gave a slightly yellow liquid (dry weight, 0.8536 g.), the infrared spectrum of which was identical to that of 1,3-propanesultam.

Repetition of this experiment using 0.9798 g. of propanesultam and 0.0483 g. of anhydrous *p*-toluenesulfonic acid gave in addition

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[13] P. Rumpf, *Compt. rend.*, **204**, 592 (1937).

[14] M. S. Kharasch, E. M. May, and F. R. Mayo, *J. Org. Chem.*, **3**, 175 (1938).

to 0.1635 g. of polymer, 0.0425 g. (55%) of purified N-*p*-toluenesulfonylpropanesultam melting at 205–206°.

C.—A small test tube charged with 0.1723 g. of anhydrous *p*-toluenesulfonic acid and 0.1221 g. of propanesultam was placed in an oil bath at a temperature of 90°. The acid dissolved readily, yielding a clear, slightly yellow solution. When the bath had been rapidly heated to 105°, the mixture suddenly solidified. The solid remained in the bath at 105–115° for 15 min. (total heating time, 20 min.). The product was then cooled, treated with 40 ml. of acetone, and filtered. The white crystalline material insoluble in acetone weighed 0.0965 g. dry, melted with decomposition at 297–300°, and was very strongly acidic. From its infrared spectrum, it was identified as the *p*-toluenesulfonic acid salt of 3-aminopropanesulfonic acid. The principal infrared absorptions (in μ) of this compound were 2.95 (b), 3.20 (s), 3.34 (s), 3.45 (m), 4.90 (m), 6.15 (m), 6.71 (m), 8.28 (s), 8.60 (s), 8.71 (s), 9.26 (s), 9.66 (s), 9.89 (s), 10.24 (m), 11.86 (m), 12.50 (s), 13.40 (m).

The acetone filtrate was evaporated to yield a sticky yellow solid. Recrystallization from anhydrous ethanol gave 0.0816 g. (30%) of white crystalline material melting at 205–206°, unchanged upon admixture with N-*p*-toluenesulfonylpropanesultam. Its infrared spectrum was identical with that of the authentic material.

Repetition of the experiment at 160° with dry nitrogen bubbling through the mixture gave in 10 min. 46% of N-*p*-toluenesulfonylpropanesultam, m.p. 205–206°, and 20% of the hydrolysis product, m.p. 297–300° dec.

N-2,5-Dimethylbenzenesulfonylpropanesultam. A.—A small test tube charged with 0.5 g. of propanesultam and 0.7 g. of anhydrous 2,5-dimethylbenzenesulfonic acid [Eastman White Label, dried overnight at 55° (0.1 mm.) over phosphoric anhydride] and purged with dry nitrogen, was heated in an oil bath at 160° for 30 min., cooled, and treated with 20 ml. of cold water. A small amount of white, crystalline solid was removed by filtration, washed with water, and recrystallized from anhydrous ethanol to give 0.05 g. (6%) of a product melting at 127–128°. It was shown to be N-2,5-dimethylbenzenesulfonyl propanesultam by its infrared spectrum, which very closely resembled that of N-benzenesulfonylpropanesultam and of N-*p*-toluenesulfonylpropanesultam.

Anal. Calcd. for $C_{11}H_{15}NO_4S_2$: C, 45.65; H, 5.22; N, 4.84. Found: C, 45.71; H, 5.40; N, 4.95.

B.—A small quantity of 2,5-dimethylbenzenesulfonic acid dihydrate (Eastman White Label) was dried at 55° at reduced pressure over phosphoric anhydride for 5 hr. To 0.0073 g. of the dried acid in a small test tube was added, under a blanket of nitrogen, 0.9960 g. of hot propanesultam which had been dried for 2 hr. at 160° in a stream of dry nitrogen. The nitrogen inlet capillary was immediately placed in the liquid, and the mixture was heated to 160° for 17.5 hr. The product was cooled, treated with 20 ml. of water, and filtered. The solid product was washed twice with 5-ml. portions of water, once with 15 ml. of acetone, and dried. The light brown powder obtained weighed 0.0936 g. and melted at 222–226° to a clear, viscous liquid. Slow evaporation of the aqueous acetone filtrate gave approximately 2 mg. of a water-insoluble crystalline solid melting at 127–128°. Comparison of the infrared spectrum with that of the N-2,5-dimethylbenzenesulfonylpropanesultam obtained in the preceding experiment showed the two to be identical.

Mesitylenesulfonic acid dihydrate, prepared from freshly distilled mesitylene and concentrated sulfuric acid by the method of Suter and Weston[15] and recrystallized from chloroform, melted at 77.5–78.0°.

Attempted Preparation of N-Mesitylenesulfonylpropanesultam.—A small test tube was charged with 0.2370 g. of mesitylenesulfonic acid dihydrate (dried overnight at 0.1 mm. over phosphoric anhydride). To the anhydrous acid was added, under a blanket of dry nitrogen, 0.1238 g. of propanesultam, which had been dried for 2 hr. at 160° in a stream of nitrogen. A rapid stream of nitrogen was passed through the mixture by means of a capillary inlet, and the tube was placed immediately in an oil bath at 160°. The mixture solidified after about 20 min. The product was cooled and treated with 10 ml. of cold water, in which it dissolved rapidly and completely with the evolution of some heat. The water was evaporated *in vacuo* at room temperature leaving a sticky, yellow solid. The solid, after extraction with acetone and drying, weighed 0.1527 g. and melted with decomposition at about 210°. It was strongly acidic and had an infrared spectrum very similar to that of the *p*-toluenesulfonic acid salt of 3-aminopropanesulfonic acid. Evaporation of the acetone extract gave a yellow acidic oil, which was not investigated.

Reaction of Benzenesulfonyl Chloride with Propanesultam.—A mixture of 0.1760 g. of benzenesulfonyl chloride and 0.1229 g. of propanesultam, when heated to 160° for 2 hr., gave, in addition to a considerable amount of unchanged benzenesulfonyl chloride, 0.0211 g. of a dark brown solid from which no N-benzenesulfonylpropanesultam could be extracted with acetone. The solid melted with decomposition at 145–150°.

Polymerization of Propanesultam.—The same general procedure was used for all of the sultam polymerizations. In a few of the experiments, the nitrogen used as a purging gas (Matheson, high purity, dry) was deoxygenated by passage through Fieser's solution,[16] and dried by concentrated sulfuric acid and phosphoric anhydride, but the water absorbed from Fieser's solution caused channeling in the phosphoric anhydride bed, and since the presence of oxygen was found to have no adverse effect on the course of the reaction, Fieser's solution was subsequently eliminated from the gas purification train. The examples given are typical of the polymerization experiments.

Base-Catalyzed Polymerization.—A side-arm rest tube was charged with 0.0103 g. (0.039 mmole) of N-benzenesulfonyl-1,3-propanesultam and 1.0987 g. (9.065 mmoles) of chromatographically pure 1,3-propanesultam. Dry nitrogen was bubbled through the mixture at room temperature until the solid had dissolved. About 3 mg. (0.1 mmole) of sodium hydride was then added, and the mixture was purged with nitrogen and shaken until all of the hydride had reacted. The mixture was then placed in an oil bath at 130° and allowed to react under nitrogen for 18 hr. At the end of that time, the mixture was cooled and the hard, slightly yellow, solid cake was removed and ground under water in a mortar. The solid was collected by centrifugation, washed twice with water, then with acetone, and dried. The product weighed 0.7181 g. (64.4% conversion, based on 1,3-propanesultam) and melted at 257–260°. Fibers, which could be cold-drawn, were pulled from the melt. The intrinsic viscosity of the polymer, determined in concentrated sulfuric acid solution, was found to be 0.77 dl./g.

Anal. Calcd. for $C_3H_7NO_2S$: C, 29.73; H, 5.82; N, 11.56. Found: C, 29.82; H, 5.65; N, 11.5.

Acid-Catalyzed Polymerization.—A side-arm test tube was charged with 0.0422 g. of mesitylenesulfonic acid dihydrate (0.0358 g. anhydrous), which was dried for 4 hr. at 0.1 mm. over phosphoric anhydride. Another tube was charged with about 3.4 g. of propanesultam of 99.1% purity (determined by v.p.c. analysis) and weighed. A stream of dry nitrogen was bubbled through the liquid by means of a capillary inlet, and the tube was placed in an oil bath at 160° for 2 hr. to dry the monomer. Dry nitrogen was then admitted to the tube containing the catalyst and the hot monomer was quickly poured in under a blanket of nitrogen. The nitrogen purge was immediately applied to the mixture and left in place during the entire 20-hr. polymerization at 160°. The tube in which the sultam had been dried was carefully wiped to remove oil and reweighed. Monomer charged was found to be 3.0514 g.

After about 5 min. at 160°, the mixture deposited a very small amount of a fine, white, crystalline solid, which redissolved after about 3 hr. After 20 hr. at 160°, a soft, white solid had formed. The product was cooled and treated with 20 ml. of cold water, producing a fine, white suspension. The solid was separated by centrifugation in a tared tube, washed four times with 20-ml. portions of water, twice with 20-ml. portions of acetone, and dried overnight at 0.1 mm. The dried solid weighed 0.5604 g. (18.4% conversion) and melted at 227–232° to a colorless, viscous liquid from which fibers could not be drawn. The intrinsic viscosity of the material in concentrated sulfuric acid solution was 0.07 dl./g. Its infrared spectrum was similar to that of the monomer, except that it lacked a medium-intensity band at 10.02 μ.

Anal. Calcd. for $C_3H_7NO_2S$: C, 29.73; H, 5.82; N, 11.56. Found: C, 29.89, 29.87; H, 5.55, 5.60; N, 11.45, 11.24.

The aqueous acetone washings from the isolation of the polymer were evaporated at reduced pressure, leaving a slightly

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[15] C. M. Suter and A. W. Weston, "Organic Reactions," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1947, p. 162.

[16] L. F. Fieser, *J. Am. Chem. Soc.*, **46**, 2639 (1924).

yellow liquid. Dried 12 hr. over phosphoric anhydride, the liquid weighed 2.3661 g. Its infrared spectrum was identical to that of 1,3-propanesultam.

Acknowledgment.—We are indebted to Mr. P. Waszeciak, who prepared a sample of chromatographically pure propanesultam by fractional melting. We also acknowledge with thanks the assistance of Dr. Sidney Siggia, Director of the Olin Central Analytical Laboratories, and his staff for the microanalyses, infrared spectra, intrinsic viscosities, and v.p.c. results reported.

Notes

The Condensation of Acetone with Dimethylfulvene[1]

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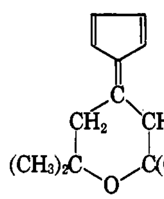
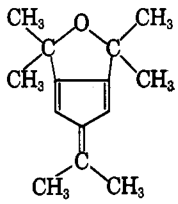
While it has been recognized for many years that cyclopentadiene will condense with more than one mole of acetone under basic conditions, it is noteworthy of the complexity of the chemistry of these compounds that no adequate proof of structure of the condensation product(s) has ever been given.[2] Thiele and Balhorn[3] reported that cyclopentadiene reacted with three equivalents of acetone and that dimethylfulvene reacted with two equivalents of acetone to give I, a structure assigned solely on the basis of elemental analysis.


I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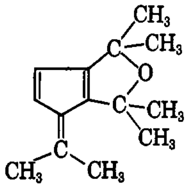

III

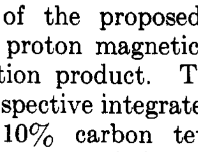
Subsequently, Ziegler and Crossman[4] modified the structure to either II or III on the basis of the related reaction of dimethylfulvene with anisaldehyde. Their argument rested on the observation that the condensation product of anisaldehyde with dimethylfulvene did not involve reaction with the methyl groups at the 6-position. Only one mole equivalent of anisaldehyde entered into the reaction.

The preparation of dimethylfulvene by the reaction of cyclopentadiene and acetone in the presence of alcoholic potassium hydroxide[5] always leads to the formation of a considerable amount of higher boiling material. Careful fractional distillation of the material at reduced pressures produced one main product (an orange oil) plus a large amount of tar. The same product was isolated when dimethylfulvene reacted with acetone in alcoholic potassium hydroxide. As will be seen subsequently, this product resulted from the addition of one mole of acetone to dimethylfulvene. Numerous repetitions of the preparation of dimethylfulvene and of the subsequent reaction of this with acetone failed to yield any evidence of a product corresponding to the condensation of two molecules of acetone per one molecule of dimethylfulvene.

The chemical analysis and hydrogenation equivalent of the condensation product from dimethylfulvene and acetone established the formula as $C_{11}H_{16}O$ with three double bonds in the molecule. The infrared spectrum indicated the presence of a hydroxyl group.

The hydrogenated product was a colorless oil, the analysis of which agrees with the formula $C_{11}H_{22}O$. This material also had a strong hydroxyl band in the infrared. The position of attachment was elucidated by subjecting the hydrogenated product to dehydration and ozonolysis yielding 3-isopropylcyclopentanone.

While these data locate the position of the acetone moiety at C-2 on the fulvene ring, the possible location of the three double bonds requires further information. The fact that the ultraviolet absorption spectra of the condensation product and of dimethylfulvene show maxima at 267 mμ (ϵ 1.8 × 10^4 and 2.2 × 10^4, respectively) suggests similar conjugated structures for both compounds. This would give structure IV as the correct formula for the condensation product.


IV

Confirmation of the proposed structure was obtained from the proton magnetic resonance spectrum of the condensation product. The following absorptions and their respective integrated proton values were observed in a 10% carbon tetrachloride solution: (1) the ring protons consisting of doublet at τ 3.61 (two protons) and a triplet at τ 3.86 (one proton); (2) a broad weak peak at τ 7.15 which was variable in position with dilution was attributed to the hydroxyl hydrogen; (3) a sharp band at τ 7.91 (6 protons); and (4) a similar band at τ 8.61 (6 protons). A detailed examination of the ring-H resonances revealed a typical AB_2 spectrum where $\sigma_A < \sigma_B$; $\nu_0\delta = -13.5$ c.p.s. The observed spectrum was analyzed by means

[1] Presented at the Southwest Regional Meeting of the American Chemical Society, Dallas, Tex., December 7, 1962.

[2] J. H. Day, *Chem. Rev.*, **53**, 167 (1953).

[3] J. Thiele and H. Balhorn, *Ann.*, **348**, 1 (1906).

[4] K. Ziegler and F. Crossman, *ibid.*, **511**, 89 (1934).

[5] G. Crane, C. E. Boord, and A. L. Henne, *J. Org. Chem.*, **67**, 1237 (1945).