zation was induced by seeding, scratching, and/or concentration.

In the case of the *o*-dimethylaminoethoxy isomer, the ethanol mother liquor was evaporated and replaced by 1-butanol before addition of the concentrated hydrochloric acid. The reduction in the case of this isomer took about 3 hr. at room temperature for 20 mmoles. The following variation increased the temperature and time required for the reaction. The amine and benzaldehyde were mixed in 50 ml. of benzene. After 2 hr., the water which separated was removed by magnesium sulfate and the benzene was removed under vacuum. Absolute ethanol was added and also removed under vacuum. The ethanol was replaced and the solution added to the reduced catalyst as above. At room temperature there was practically no hydrogen uptake at atmospheric pressure or at 50 lbs. pressure. At about 60–75°, several hours were required.

1-[(2-Dialkylaminoethoxy)phenyl]-2-benzylmethylamino-1-propanol (*X*, *R′* = *benzyl*, *R″* = *methyl*). In a manner similar to the methylation of the primary amine to give the dimethylamine, the benzylamine was methylated using formic acid and formaldehyde.

1-[(2-Dialkylaminoethoxy)phenyl]-2-dimethylamino-1-propanol (*X*, *R′* = *R″* = *methyl*). A solution of 20 mmoles of the primary amine base, 200 mmoles of 98–100% formic acid and 250 mmoles of formaldehyde as its 40% aqueous solution, was kept in a bath at 120° for about 3 hr. and at 145° for about the same length of time. To the reaction mixture was added 6 ml. of concentrated hydrochloric acid. The residue obtained on evaporation to dryness on a steam bath under vacuum was taken up in concentrated hydrochloric acid and again evaporated to dryness. The residue was now crystallized and recrystallized from the appropriate solvent.

1-[2-(2-Dimethylaminoethoxy)phenyl]-2-dimethylamino-1-propanol (*V or X*, *R* = *R′* = *R″* = *methyl*) was also obtained, as described above, *via o*-(2-dimethylaminoethoxyphenyl)-α-bromopropiophenone hydrobromide.

1-[(2-Dialkylaminoethoxy)phenyl]-2-isopropylamino-1-propanol (*X*, *R′* = *isopropyl*, *R″* = *hydrogen*). To a suspension obtained by reducing 200 mg. of platinum oxide in 25 ml. of alcohol was added a day-old solution of 20 mmoles of the primary amine and 25 mmoles of acetone. After uptake of the theoretical quantity of hydrogen, the reaction mixture was concentrated to dryness. In all but the *p*-diethylaminoethoxy isomer (an oil), solid free bases were obtained as residues. The residues were dissolved in the solvent from which the salt was to be recrystallized and the appropriate hydrogen halide was added.

1-[(2-Dialkylaminoethoxy)phenyl]-2-diethylamino-1-propanol (*X*, *R′* = *R″* = *ethyl*). To a solution of 20 mmoles of the primary amine in 50 ml. of absolute ethanol was added 20 mg. of platinum oxide and 50 mmoles of freshly distilled acetaldehyde while keeping the reaction flask in an ice bath. Hydrogen was introduced with shaking at atmospheric pressure and temperature until no further hydrogen uptake occurred. An additional 50 mmoles of acetaldehyde was added and reduction again continued until cessation of hydrogen uptake. The catalyst was removed by filtration. The residue obtained on evaporation of the filtrate, was taken up in 2-propanol and made acid to Congo Red with hydrogen bromide or hydrogen chloride. The resulting solid was recrystallized.

1-[2-(2-Dimethylaminoethoxy)phenyl]-2-diethylamino-1-propanol (*V or X*, *R* = *methyl*, *R′* = *R″* = *ethyl*) was prepared in this way, and also as described above *via o*(2-dimethylaminoethoxyphenyl)-α-bromopropiophenone hydrobromide.

1[4-(2-Dimethylaminoethoxy)phenyl]-2-ethylamino-1-propanol dihydrochloride (*X.2HCl*, *R* = *methyl*, *R′* = *ethyl*, *R″* = *hydrogen*). This was prepared in the same way that *1*-[4-(2-dimethylaminoethoxy)phenyl]-2-diethylamino-1-propanol was prepared except that the second reduction in the presence of acetaldehyde was omitted. Repeated recrystallization from ethanol-methanol solvent gave 25–30% yield of product which showed no primary amine by Van Slyke analysis and analyzed as expected for the monoethylated product.

MORRIS PLAINS, N. J.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Beckmann Rearrangement of Some Cyclic Sulfone Ketoximes[1]

WILLIAM E. TRUCE AND JOHN A. SIMMS[2]

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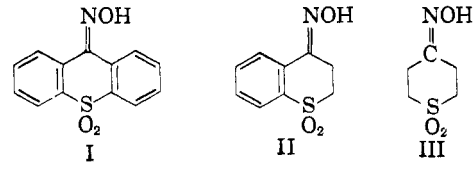
The ease of rearrangement of thiaxanthone 5,5-dioxide oxime (I), 4-thiachromanone 1,1-dioxide oxime (II), and tetrahydro-1,4-thiapyrone 1,1-dioxide oxime (III) was found to be III ≫ II ≅ I. The rearrangement product of I was characterized by independent synthesis.

It has been show that some heterocyclic ketoximes undergo the Beckmann rearrangement to give the expected lactams.[3-5] However, all of the ketoximes previously examined had the ketoxime function separated from the hetero atom by saturated carbon atoms. It was felt that an appreciable change in reactivity might result if the hetero atom was conjugated with the oxime group.

Therefore, the three cyclic sulfone ketoximes, thiaxanthone 5,5-dioxane oxime (I), 4-thiachromane 1,1-dioxide oxime (II), and tetrahydro-1,4-thiapyrone 1,1-dioxide oxime (III), were prepared and the conditions necessary for their rearrangement were determined.



I II III

(1) Taken from Mr. Simms' Ph.D. Thesis, Purdue University, 1956.

(2) Dow Chemical Company Fellow, 1954–1955.

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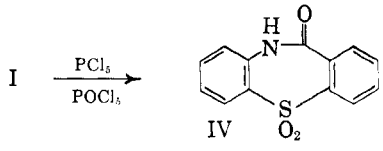
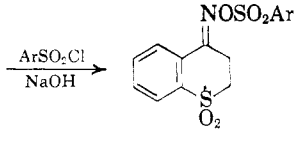
Oxime I was synthesized from the known ketone, thiaxanthone 5,5-dioxane.[6-8] A 70% yield of the normal rearrangement product, the lactam of 2-(2′-aminobenzenesulfonyl)benzoic acid (IV), was isolated after refluxing a mixture of I with phosphorus pentachloride and phosphorus oxychloride for 48 hr.



Compound IV is easily hydrolyzed, but the 2-(2′-aminobenzenesulfonyl)benzoic acid (V) obtained re-cyclized upon drying at 100°. The independently synthesized[9] V behaved similarly, and it appears that the melting point observed is for the lactam rather than for the free amino acid.

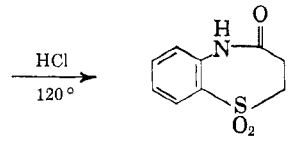
4-Thiachromanone 1,1-dioxide[10] was prepared from thiophenol and β-chloropropionic acid. Its oxime (II) forms more easily than the oxime of thiaxanthrone 5,5-dioxide. 4-Thiachromanone 1,1-dioxide oxime (II) did not rearrange when it was treated with a number of acid catalysts. Treatment of the oxime in refluxing phosphorus oxychloride with phosphorus pentachloride resulted in tar formation; no reaction was observed with phosphorus pentachloride in diethyl ether. The oxime was isolated unrearranged from concentrated sulfuric acid, although it was hydrolyzed to 4-thiachromanone 1,1-dioxide by 85% sulfuric acid. Polyphosphoric acid caused extensive tar formation.

4-Thiachromanone 1,1-dioxide oxime (II) formed stable N-arylsulfonates in good yield.



The benzenesulfonate (VI) was recovered quantitatively after 6 hr. heating at 100° in methanol solution. Under similar conditions, benzophenone oxime *N*-benzene sulfonate is completely rearranged in 10 min.[11]

When VI was heated with polyphosphoric acid, or concentrated hydrochloric acid, only intractable oils were obtained. However, it was possible to rearrange the *o*-nitrobenzenesulfonate (VII) with concentrated hydrochloric acid. The lactam of



2-(2′-aminobenzenesulfonyl)propionic acid[12] (VIII) was produced in 43% yield. The configuration assigned to the 4-thiachromanone 1,1-dioxide oxime (II) is consistent with the structure of the rearrangement product, using the concept of *trans* rearrangement.[11, 11a]

Tetrahydro-1,4-thiapyrone 1,1-dioxide oxime[12b] (III) was prepared in 90% yield from the corresponding ketone.[13] When it was heated for 3 min. with 85% sulfuric acid, all the oxime dissolved without any discoloration of the solution. Chloroform extraction after neutralization with potasssium hydroxide did not separate the product. The solution was then evaporated to dryness and the residue extracted with methanol in a soxhlet extractor. An organic salt containing potassium but no sulfate was thus separated. Although this material was not further characterized, it is probably potassium 2-(2′-aminoethylsulfonyl)propionate. Tetrahydro-1,4-thiapyrone-1,1-dioxide oxime (III) had been rearranged with polyphosphoric acid[12b] but the product was not isolated.

Electron withdrawing groups introduced into the acetophenone portion of substituted acetophenone oximes[14] or acetophenone oxime picryl ethers[15] caused the Beckmann rearrangement to proceed much more slowly than in the unsubstituted compounds.

A similar deactivating effect is observed in the rearrangement of thiaxanthone 5,5-dioxide oxime (I). This compound was even less reactive than anthraquinone monoxime[16,17] (45 hr. *vs.* 5 hr. under the same reaction conditions for complete rearrangement).

A direct comparison of the relative rates at which thiaxanthone 5,5-dioxide oxime (I) and 4-thiachromanone 1,1-dioxide oxime (II) rearrange could not be made because of the decomposition of the latter oxime when it was refluxed with phosphorus pentachloride in phosphorus oxychloride in phosphorus oxychloride solution. It can be estimated from the vigor of the conditions necessary to obtain rearrangement of the corresponding *o*-nitrobenzenesulfonate that 4-thiachromanone 1,1-dioxide oxime is approximately equal to thiaxan-

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thione 5,5-dioxide oxime in resistance to rearrangement.

Tetrahydro-1,4-thiapyrone-1,1-dioxide oxime (III) rearranges very readily when treated with 85% sulfuric acid. 4-Thiachromanone 1,1-dioxide oxime (II) is isolated in good yield after heating for 1 hr. with concentrated sulfuric acid, thus making the ease of rearrangement in this series: tetrahydro-1,4-thiapyrine-1,1-dioxide oxime (III)$\gg$4-thiachromanone-1,1-dioxide oxime (II) $\cong$thiaxanthone 5,5-dioxide oxime (I).

EXPERIMENTAL[18]

Thiaxanthone 5,5-dioxide Oxime (I). Thiaxanthone was prepared from benzene and thiosalicyclic acid in 68% yield as a light yellow solid (m.p. 213–214°; lit.[7] 209°) by the method of Davis and Smiles[7] using the more specific directions given by Gomberg and Britton.[8] It was oxidized with a solution of hydrogen peroxide in acetic acid according to Ullmann.[6] A quantitative yield of thiaxanthone 5,5-dioxide, m.p. 187–188.5° (lit.[6] 187°), was obtained.

The oxime was produced when a mixture of 10 g. (0.041 mole) of thiaxanthone 5,5-dioxide, 16 g. (0.24 mole) of hydroxylamine hydrochloride, and 30 ml. (0.37 mole) of pyridine in 150 ml. of ethyl alcohol was refluxed for 23 hr. The clear solution that resulted was cooled and poured into ice water. The precipitate that formed was filtered and washed well with hot water to remove any occluded pyridine hydrochloride. The dried oxime, 9.6 g. (92%), m.p. 209–211°, was recrystallized from absolute ethanol in two fractions: (1) 6.5 g., m.p. 213–214°; (2) 1.6 g., 213–213.5°.

Anal. Calcd. for $C_{13}H_9O_3NS$: C, 60.23; H, 3.50; N, 5.40. Found: C, 60.32; H, 3.82; N, 5.27.

Shorter reaction times produced a mixture containing unreacted thiaxanthone 5,5-dioxide.

Beckmann rearrangement of thiaxanthone 5,5-dioxide oxime. A solution of 10.2 g (0.048 mole) of phosphorus pentachloride in 75 ml. of phosphorus oxychloride was rapidly added to a solution of 9 g. (0.034 mole) of thiaxanthone 5,5-dioxide oxime in 125 ml. of phosphorus oxychloride. After the clear yellow mixture had been refluxed for 48 hrs, 100 ml. of solvent was removed and the cooled residue was poured into ice water with vigorous stirring. The yellow oil which precipitated decomposed to give a yellow white solid. Extraction of the filtrate with ether yielded some more solid. The combined solids were heated for 1 hr. with 300 ml. of 50% sulfuric acid to complete the decomposition of the rearrangement complex. The sulfuric acid mixture was cooled and the product (8.1 g.; m.p. 200–275°) recovered by filtration. It was heated for 1.5 hr. with 300 ml. of 7% sodium hydroxide. The alkali-insoluble residue (0.9 g.; m.p. 187–189°) was identified as thiaxanthone 5,5-dioxide. The filtrate was acidified and the precipitate (6.3 g., m.p. 284–294°) that formed was separated by filtration and dried. It was recrystallized from a mixture of ethanol and acetic acid in three fractions: (1) 1.1 g., m.p. 291–292.5°; (2) 1.5 g., 289–291°; (3) 1.7 g., 289.5–290°. A mixture of fraction 1 and 2-(2′-aminobenzenesulfonyl)benzoic acid (m.p. 287–288°) melted sharply at 289°. It is probable that this is the melting point of the corresponding lactam. An analytical sample cyclized when it was dried under vacuum in an Abderhalden apparatus at 100° for 15 hr.

Anal. Calcd. for $C_{13}H_{11}NO_4$: C, 56.31; H, 4.00; N, 6.05. Calcd. for $C_{13}H_9NO_3$: C, 60.32; H, 3.82; N, 5.27. Found: C, 59.90; H, 4.08; N, 5.42.

The yield of rearrangement product dropped when a reflux time of 16 hr. was used. More thiaxanthone 5,5-dioxide was also isolated.

2-(2′-Aminobenzenesulfonyl)benzoic acid.[9] This compound was prepared in low yield by a three-step synthesis starting with *o*-thiosalicylic acid and *o*-nitrochlorobenzene.

o-Thiosalicylic acid (50 g., 0.325 mole) was added to a solution prepared by dissolving 15.0 g. (0.65 mole) of sodium in 300 ml. of absolute ethanol. A solution of 51 g. (0.324 mole) of *o*-nitrochlorobenzene in 300 ml. of absolute ethanol was then added and the mixture refluxed, with stirring, for 4 hr. The solid that formed was collected, dissolved in water, and filtered. When the filtrate was acidified with hydrochloric acid, a dark, tarry solid precipitated. It was precipitated from alcoholic solution with water and then recrystallized from chloroform to produce 28.8 g. (33%) of 2-carboxyphenyl 2′-nitrophenyl sulfide as a brown solid, m.p. 166–169°.

The above sulfide (24 g., 0.0875 mole) was dissolved in 200 ml. of glacial acetic acid and 29 ml. (0.252 mole) of 30% hydrogen peroxide was added at a rate such that gentle reflux was maintained. After an additional three-hour reflux period, the solution was concentrated to yield 2-(2′-nitrobenzenesulfonyl)benzoic acid, wt. 21.5 g. (85%), m.p. 198–200°.

The 2-(2′-nitrobenzenesulfonyl)benzoic acid (10 g., 0.025 mole) was suspended in 200 ml. of concentrated hydrochloric acid and the mixture was heated to reflux. Tin (1.7 g) was carefully added so as to minimize the initial vigorous reaction. The remaining tin (22 g. a total of 0.206 nole) was added in small portions and the mixture heated on the steam cone for 3 hr. The product (8.9 g., m.p. 284–288°) precipitated from the cooled reaction mixture. It was recrystallized from a mixture of ethanol and acetic acid in three fractions: (1) 4.7 g., m.p. 287–289°; (2) 1.3 g., m.p. 285–287°; (3) 0.7 g., m.p. 280–285°. A sample for analysis (m.p. 287–288°) was recrystallized three times from the same solvent mixture and then dried in a Abderhalden apparatus at 100° for 15 hr. This amino acid evidently cyclized during the drying operation to form the corresponding lactam.

Anal. Calcd. for $C_{13}H_{11}NO_4S$: C, 56.31; H, 4.00; N, 5.05. Calcd. for $C_{13}H_9NO_3S$: C, 60.32; H, 3.82; N, 5.27. Found: C, 59.46; H, 3.87; N, 5.30.

4-Thiachromanone 1,1-dioxide. This sulfone was prepared from *β*-chloropropionic acid and thiophenol *via* *β*-phenylmercatopropionic acid (83% yield) and thiachromanone (68% yield) by the method of Arndt.[10] Oxidation with hydrogen peroxide in acetic acid produced 4-thiachromanone sulfone (m.p. 128–129.5°; lit.[10] 131–132°) in 64% yield.

4-Thiachromanone sulfone oxime (II). A solution of 20 g. (0.0102 mole) of 4-thiachromanone sulfone, 42.8 g. (0.612 mole) of hydroxylamine hydrochloride, and 74 ml. (0.918 mole) of pyridine in 500 ml. of absolute ethanol was refluxed for 45 hr. The solution was concentrated to 300 ml. and then poured into ice water. The precipitate was washed with three 100 ml. portions of hot water leaving a residue of 19.0 g. (m.p. 189–192°) of grey white solid. Ether extraction of the filterate and wash water yielded, after recrystallization from water, an additional 4.5 g. (m.p. 187–189°) of oxime. Recrystallization of the combined fractions from water gave 19.1 g. (82%) of oxime, m.p. 191–192°. The analytical sample melted at 193.5–194.5° after three more recrystallizations from water.

Anal. Calcd. for $C_9H_9O_3NS$: C, 51.17; H, 4.29; N, 6.63. Found: C, 51.12; H, 4.31; N, 6.95.

Attempted Beckmann rearrangement of 4-thiachromanone 1,1-dioxide oxime. None of the expected rearrangement product, the lactam of 2-(2′-aminobenzenesulfonyl)propionic acid, was isolated in any of the experiments outlined in Table 1. The catalysts caused tar formation, or hydrolysis to thiachromanone 1,1-dioxide as the principle reactions observed. In a number of cases the oxime was recovered. It is very resistant to hydrolysis or rearrangement when heated with concentrated sulfuric acid. Less concentrated sulfuric acid (85%) causes rapid hydrolysis to 4-thiachromanone 1,1-dioxide.

4-Thiachromanone 1,1-dioxide oxime N-benzenesulfonate (VI). 4-Thiachromanone 1,1-dioxide oxime (6.33 g., 0.03

(18) All melting points are uncorrected.

TABLE 1

Expt.[a]	Catalyst	Solvent	Reaction Time and Temperature	Products Isolated
1	PCl_5	$POCl_3$	4 hrs. at 25° 21 hrs. at reflux	Tar and recovered oxime
2	PCl_5	Ethyl ether	12 hrs at 25°	70% recovery of oxime
3	PCl_5	Ethyl ether	6 days at reflux	Low yield of thiachromanone 1,1-dioxide
4	PCl_5	$CHCl_3$	14 hrs. at 25°, 24 hrs. at reflux	Mixture of oxime and thiachromanone 1,1-dioxide
5	85% H_2SO_4	85% H_2SO_4	3 min. on steam plate	65% Yield of thiachromanone 1,1-dioxide
6	93% H_2SO_4	93% H_2SO_4	1 hr. on steam plate	83% Recovcovery of oxime
7	Polyphosphoric acid	Polyphosphoric acid	6 min. at 115°	Tar and recovered oxime

[a] All these experiments were run on 2 g. samples of the oxime.

mole) was mixed with 225 ml. of water and 5.55 g. (0.0315 mole) of benzenesulfonylchloride was added. After the rapid addition of 33 ml. of 1*N* sodium hydroxide solution, the mixture was stirred for 19 hr. at room temperature and then refluxed for 1 hr. Dilution with water and cooling caused the precipitation of 6.05 g. (m.p. 144–147°), 57% of light brown solid. The pure benzenesulfonate, obtained by recrystallization from methanol and then from a mixture of ether and chloroform, was a white crystalline solid (m.p. 150.5–151°).

Anal. Calcd. for $C_{15}H_{13}NS_2O_5$: C, 51.28; H, 3.72; N, 3.98. Found: C, 51.04; H, 3.90; N. 3.85.

This oxime sulfonate did not rearrange when it was heated with polyphosphoric acid for 0.5 hr. at 140°. The product contained 20% of the starting oxime sulfonate, as well as a considerable quantity of tar. The oxime sulfonate was recovered quantitatively after 6 hr. heating at 100° in methanol solution in a sealed tube. Concentrated hydrochloric chloric acid, with heating at 120° for 3 hr., produced only tar.

Thiachromanone 1,1-dioxide oxime o-nitrobenzenesulfonate (VII). Using the same procedure given above, 2.10 g. (0.01 mole) of thiachromanone sulfone oxime and 2.33 g. (0.01 mole) of *o*-nitrobenzenesulfonyl chloride[19] yielded 3.52 g. (m.p. 179–180°) of the corresponding *o*-nitrobenzenesulfonate. After four recrystallizations from a mixture of dioxane and water, this material melted with decomposition at 182.5°. The analytical results indicate that it was still rather impure.

Anal. Calcd. for $C_{15}H_{12}O_7N_2S_2$: C, 45.45; H, 3.03; N, 7.08. Found: C, 43.92; H, 2.50; N. 5.62.

Rearrangement of 4-thiachromanone 1,1-dioxide o-nitrobenzenesulfonate. The oxime sulfonate (0.90 g., m.p. 180–181°) was heated with 40 ml. of concentrated hydrochloric acid in a sealed tube at 120° for 12 hr. The resulting dark brown mixture was poured into ice water and the precipitate (0.10 g., m.p. 169–179°) of unrearranged sulfonate filtered off. The oil that was obtained by concentrating the filtrate under an air jet was dissolved in methanol and ether was added. A dark brown crystalline material (wt. 0.21 g., m.p. 234–240°, 43% yield) precipitated. The 2-(2′-aminobenzenesulfonyl)propionic acid lactam was purified by another precipitation from ethanol solution with ether; m.p. 243–244° (lit.[12] m.p. 246–247°).

Tetrahydro-1,4-thiapyrone-1,1-dioxide. Tetrahydro-1,4-thiapyrone (m.p. 60–63°; lit.[19] m.p. 65–66°) was prepared in 10% yield by the Dieckmann condensation of methyl β-thiodipropionate.[20] It was oxidized to the corresponding sulfone (m.p. 171°, lit.[13] 170°) in 90% yield with 30% hydrogen peroxide in glacial acetic acid.

Tetrahydro-1,4-thiapyrone 1,1-dioxide oxime[12] (III). A mixture of 3.6 g. (0.24 mole) of tetrahydro-1,4-thiapyrone 1,1-dioxide, 2.1 g. (0.29 mole) of hydroxylamine and 2.6 g., (0.024 mole) of sodium carbonate in 150 ml. of water was heated to reflux and then was allowed to stand for 11 hr. The reaction mixture was evaporated to dryness and the residual solid extracted with chloroform in a Soxhlet extractor for 72 hr. Evaporation of the extract yielded 1.57 g. (m.p. 197–201°; lit.[12] 197–198°) of the oxime.

Rearrangement of the oxime of tetrahydro-1,4-thiapyrone 1,1-dioxide oxime. The *Organic Synthesis* procedure[21] for cyclohexanone oxime was followed, although the product was too soluble to be isolated as suggested.

The oxime (1.5 g.) was heated with 12 ml. of 85% sulfuric acid for 2 min. The clear colorless solution was poured into water, cooled, and made alkaline with potassium hydroxide. The precipitate of potassium sulfate was filtered off and the filtrate was extracted three times with chloroform. No residue remained after the evaporation of the chloroform. Evaporation of the water solution yielded a solid which was extracted with methyl alcohol in a Soxhlet extractor for 20 hr. Evaporation of the extract yielded 1.76 g. of white crystalline solid. This material chars but does not melt. It gives a negative sulfate ion test with barium chloride and shows a strong potassium flame when it is burned. Although this material was not further characterized, it is probably potassium 2-(2′-aminoethylsulfonyl)propionate.

LAFAYETTE, IND.

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