the formation of a substance far more soluble in ether and benzene than the original compound. It is proposed to examin this reaction further.

Distillation of the Reduction Product with Zinc Dust.—An attempt was made to reduce the substance still further by distilling with zinc dust, this method having been used by v. Baeyer in converting oxindole into indole; as a result an oily mixture of substances was obtained from which colorless leaflets separated which were found to be carbazole. The oily substance formed at the same time showed most intense blue-red fluorescence but was present in quantities too small to admit of identification.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF SWARTHMORE COLLEGE.]

THE ACTION OF ETHYL ALCOHOL ON PARATOLUIDINE DIAZONIUM HYDROCHLORIDE AND OF SULFURIC ACID ON THE ETHYL ETHER OF PARACRESOL.

BY PERCIVAL RUDOLPH ROBERTS AND GELLERT ALLEMAN.

Received January 2, 1911.

Some years ago, one of us[1] studied the action of methyl alcohol on paratoluidine diazonium sulfate and the effect of sulfuric acid on the methyl ether of paracresol. It was thought that the ethyl ether of paracresol could be obtained in a like manner, and with no more difficulty than attended the preparation of the corresponding methoxy compound. Numerous failures to secure a good yield of the ethoxy product led to changes in the methods and conditions incident to the production of the material desired. Owing to the fact that paratoluidine sulfate is much less soluble in ethyl alcohol than is paratoluidine hydrochloride, the latter compound was employed.

Preparation of the Diazonium Compound.—Two hundred grams of Kahlbaum's paratoluidine were melted in 400 cc. of hot water, and 400 cc. of fuming hydrochloric acid gradually added. During the addition of the acid, the mixture was stirred in order to dissolve the hydrochloride formed. As soon as complete solution took place, the material was cooled by immersing the beaker containing it in cold water. The paratoluidine hydrochloride separated, on cooling, in perfectly white crystals. The supernatant liquid was decanted, the crystals thrown on a funnel fitted with a platinum cone, and the adhering water and acid removed by filtering under diminished pressure. The crystals were then placed on an unglazed porcelain plate to facilitate drying. They were used within an hour of the time they were removed from the liquid, because the color of the crystals changed, on standing over night, which indicated that, within a short time, some decomposition resulted. The crystals, which

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[1] Alleman, *Am. Chem. J.*, 31, 24 (1904).

were slightly moist, were dissolved in 99 per cent. ethyl alcohol, and the resulting solution placed in tall, narrow gas-washing bottles, holding about 500 cc. Two cylinders were connected in series. They were then packed in a mixture of ice and salt and cooled to —25°. Nitrogen trioxide, generated by treating lump arsenic trioxide with nitric acid of 1.35 sp. gr., was first cooled by passing it through two gas-washing bottles surrounded by ice water, and then conducted into the bottles containing the alcoholic solution of the paratoluidine hydrochloride. During the passage of the gas, the temperature of the latter named solution was not permitted to rise above —15°. This was easily regulated by closely watching the supply of the entering gas, and by a liberal use of ice and salt. Within twenty minutes the alcoholic solution turned red, and the diazotization was completed in about one hour—the time depending upon the rapidity of the flow of nitrogen trioxide. The end of the reaction could be easily determined by removing a small portion of the alcoholic solution and adding a solution of sodium hydroxide to it. In case the hydrochloride had not been completely diazotized, a distinct odor of paratoluidine was noticed after the addition of an excess of the sodium hydroxide solution. Frequently, at the end of the diazotizing process, a separation of two distinct liquids was noticed in the gas-washing bottle. This was especially noticeable when the temperature was kept very low and a large amount of nitrogen trioxide passed through the solution. On examination, the top layer was found to be composed of ethyl nitrite, but it was noticed also that the formation of this layer was always indicative of a larger yield of the desired product than could be obtained when the formation of the ethyl nitrite did not take place. The diazotized material did not separate from the alcohol at —25° and no attempts were made to precipitate it.

Decomposition of the Diazonium Compound.—The whole solution was transferred to a five-liter balloon flask connected with a long condenser, the balloon flask placed on a steaming water bath, and the decomposition of the diazonium compound immediately begun. The first noticeable change was in color; the light transparent wine-red solution changed to one dark and opaque. Then the solution began to foam, the foam being white for a few minutes, after which this first reaction apparently lessened in intensity for a short time. A second and much more violent reaction followed, and the color changed to a green-black. Frequently the decomposition had to be checked by pouring cold water on the balloon flask, or the whole solution would be lost through the condenser tube. Several fires resulted from the ignition of the alcohol, which was shot out of the condenser tube on certain occasions, and others from the alcohol scattered in consequence of flasks broken from sudden shock during the too rapid decomposition of the diazo compound. Fires were subsequently prevented by extinguishing all the flames in the room in which the decomposition was effected as soon as it was well under way. The decomposition was completed in about twenty minutes. The solution was then boiled for twenty minutes, after which the return condenser was replaced by a Hempel tube 1 meter long, the latter connected with a condenser, and the excess of alcohol distilled off. Considerable toluene passed over with the alcohol and the last portion had a distinct odor of ethyl ether. The residue in the balloon flask was then mixed with five times its volume of water. A dark oil separated, and the whole was heated and subjected to distillation with steam. A light lemon-yellow oil passed over and was condensed with the water in which it is practically insoluble. The oil was separated from the water by means of a separating funnel, and transferred to a flask containing fused calcium chloride. After drying for three days in this manner, it was filtered through glass wool into a distilling bulb, and fractioned. This oil has an intensely sweet and penetrating odor. It stains the skin yellow, and, after a time, on exposure to air, the odor changes and is suggestive of fresh horse manure. The average yield was about 35 per cent. of the theoretical.

After three distillations, 698 grams of oil were obtained, which boiled between 185° and 195°. 455 grams of the above distilled between 185° and 191° and 360 grams between 187° and 191°. The latter material was made use of in the following experiments. The refractive index of the latter fraction at 15° was 1.51069. The oil is very soluble in methyl alcohol, ethyl alcohol, ether, toluene and benzene. It is lighter than water.

This is evidently the paraethoxytoluene obtained by Engelhardt and Latschinow.[1]

Paraethoxymetatoluenesulfonic Acid.—Two hundred grams concentrated sulfuric acid were added to 100 grams of the paraethoxytoluene. A slight change in color, and the development of considerable heat, indicated that a reaction had taken place at the ordinary temperature, and without the application of heat. After three hours, on cooling, yellow crystals were obtained. These were removed from the solution, placed on a porous draining plate, and dried. The material was afterwards crystallized from absolute alcohol, in order to free it from any unchanged paraethoxytoluene and free sulfuric acid. From the alcoholic solution, beautiful, transparent, colorless crystals were obtained. They suggest hopper-shaped salt crystals; however, they are not isometric, but probably monoclinic. Crystals 1 cm. by 2 mm. were obtained. They melt sharply at 92–92.5°. The method just indicated furnishes a purer sulfonic acid than was obtained by first making the barium salt of the acid and then

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[1] *Z. für Chem.*, 1869, 619.

obtaining the free acid from the latter. The free sulfonic acid is extremely soluble in water, methyl alcohol, ethyl alcohol, and acetone. It is practically insoluble in ether, chloroform, carbon tetrachloride, benzene, benzine, toluene and ligroin.

The properties of the sulfone chloride and sulfonamide indicate that the sulfonic acid group enters in the meta position.

Salts of p-Ethoxytoluenemetasulfonic Acid. Barium Salt, $(C_6H_3(CH_3)(OC_2H_5)(SO_3))_2Ba.4H_2O$.—The mixture of the monosulfonic acid and sulfuric acid was dissolved in water, heated, neutralized with barium carbonate, and filtered to remove the barium sulfate. The barium sulfonate crystallizes in large flakes which are lustrous and suggest, in appearance, boric acid. On standing during the summer vacation, the solution evaporated, leaving crystals of the barium sulfonate about 3 cm. in length and 1 cm. in thickness. The salt does not effloresce on long exposure to air. After repeated crystallization of this salt, the following results were obtained, on analysis:

Calculated for $(C_9H_{11}O_4S)_2Ba.4H_2O$: Ba, 21.48; H_2O, 11.26.
Found: Ba, 21.47, 21.45; H_2O, 11.22, 11.26.

The barium salt is quite soluble in cold water.

A large quantity of the pure free acid was obtained by exactly precipitating the barium in the barium salt of the sulfonic acid by means of dilute sulfuric acid.

Potassium Salt, $C_6H_3(CH_3)(OC_2H_5)SO_3K.H_2O$.—This salt was prepared by exactly neutralizing a hot aqueous solution of the free sulfonic acid with potassium carbonate. Large transparent, colorless monoclinic prisms were obtained, some being 4 cm. long and 4 mm. in thickness. The salt does not effloresce on long exposure to air. It is quite soluble in water.

Calculated for $C_9H_{11}O_4SK.H_2O$: K, 14.32; H_2O, 6.59.
Found: K, 14.43, 14.21; H_2O, 6.62, 6.71.

Sodium Salt, $C_6H_3(CH_3)(OC_2H_5)SO_3Na.H_2O$.—The sodium salt was made from the free sulfonic acid by exactly neutralizing an aqueous solution of the acid with sodium carbonate. Distinct colorless monoclinic prisms 6 mm. by 3 mm. by 2 mm. separated. The salt is quite stable and does not effloresce upon exposure to air. It is quite soluble in water.

Calculated for $C_9H_{11}O_4SNa$: Na, 9.00; H_2O, 7.03.
Found: Na, 8.93, 9.07; H_2O, 7.10, 7.13.

The salt, when heated for a long time, readily decomposes at a temperature slightly higher than 125°.

Calcium Salt, $(C_6H_3(CH_3)(OC_2H_5)SO_3)_2Ca.7H_2O$.—The calcium salt was prepared by neutralizing a boiling aqueous solution of the free acid with finely powdered Iceland spar. Yellow-white, transparent glistening needles separated, which, on recrystallization, lost their yellow tinge. The salt is moderately soluble in water and is quite stable on exposure to air.

Calculated for $(C_9H_{11}O_4S)_2Ca.7H_2O$: Ca, 6.72; H_2O, 21.13.
Found: Ca, 6.74, 6.63; H_2O, 21.18, 21.03.

Zinc Salt, $(C_6H_3(CH_3)(OC_2H_5)SO_3)_2Zn.6H_2O$.—Zinc oxide was added to a hot aqueous solution of the free sulfonic acid. After filtering off the excess of zinc oxide and evaporating, white needles separated. These crystals are stable in air. When crushed between the fingers, they have a greasy feeling suggestive of zinc stearate.

Calculated for $(C_9H_{11}O_4S)_2Zn.6H_2O$: Zn, 10.83; H_2O, 17.90.
Found: Zn, 10.82, 10.93; H_2O, 17.77, 18.07.

Nickel Salt, $(C_6H_3(CH_3)(OC_2H_5)SO_3)_2Ni.5H_2O$.—The nickel salt was made by neutralizing the free sulfonic acid with nickel carbonate. It forms small well defined crystals which have a very slight light green tint. The salt is stable when exposed to air. Difficulty was experienced in the determination for water as it apparently decomposes about the time it loses its last trace of water.

Calculated for $(C_9H_{11}O_4S)_2Ni.5H_2O$: Ni, 10.13; H_2O, 15.55.
Found: Ni, 10.11, 10.16; H_2O, 15.48, 15.58.

Copper Salt, $(C_6H_3(CH_3)(OC_2H_5)SO_3)_2Cu.6H_2O$.—In preparing this copper salt by treating the free acid with freshly prepared copper oxide, a peculiar effect was noticed. The copper oxide was entirely free from alkali but when the black oxide was added to the free acid and the mixture heated, the black oxide of copper changed to a slate color, and the latter did not subsequently dissolve. The copper salt crystallizes in distinct unattached monoclinic prisms 15 mm. by 5 mm. by 3 mm. The twin crystals were much larger. The crystals are perfectly transparent, almost colorless, with a suggestion of a blue tinge.

Calculated for $(C_9H_{11}O_4S)_2Cu.6H_2O$: Cu, 10.57; H_2O, 17.95.
Found: Cu, 10.96, 10.71, 10.44; H_2O, 18.00, 18.02, 18.07.

Copper Salt, $(C_6H_3(CH_3)(OC_2H_5)SO_3)_2Cu.12H_2O$.—Another copper salt was made by precipitating the barium from the barium salt by means of copper sulfate. Light bluish needles were obtained, which were readily soluble in water.

Calculated for $(C_9H_{11}O_4S)_2Cu.12H_2O$: Cu, 8.95; H_2O, 30.44.
Found: Cu, 8.77, 8.82; H_2O, 30.42, 30.39.

Lead Salt, $(C_6H_3(CH_3)(OC_2H_5)SO_3)_2Pb.6H_2O$.—Made by neutralizing the free acid with freshly prepared lead hydroxide. Large white crystals were obtained, which on exposure to air lost their luster, without apparently losing water of crystallization. The salt strongly suggests a change in crystal system on exposure to air as in the case of crystals of sulfur.

Calculated for $(C_9H_{11}O_4S)_2Pb.6H_2O$: Pb, 27.72; H_2O, 14.48.
Found: Pb, 27.76, 27.57; H_2O, 14.53, 14.69.

All of the above salts have a much stronger crystallizing force and are much less soluble in water than the corresponding salts of paramethoxymetatoluenesulfonic acid prepared and described by Alleman.[1]

We are indebted to Mr. R. L. Hill, of this laboratory, for assistance in connection with the purification and analysis of the lead and copper salts.

The evidence showing that the sulfonic acid entered in the meta position will be presented in a subsequent paper.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

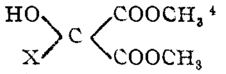
CONDENSATIONS IN THE MESOXALIC ESTER SERIES.

BY RICHARD SYDNEY CURTISS AND EARLE K. STRACHAM.

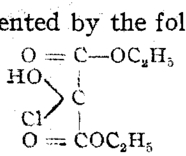
Received January 19, 1911.

The methods hitherto used for making ethyl oxomalonate, $O = C = (CO_2C_2H_5)_2$, have given a product which is a mixture of this substance with ethyl dihydroxymalonate. To produce the former substance in a state of purity it is necessary to distil ethyl dihydroxymalonate with phosphorus pentoxide.[2] Thus we have prepared this substance, a very reactive green oil, and have studied its carbonyl reactions, following them by the interesting, and more or less rapid change of color.[3]

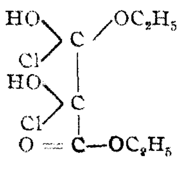
We have first investigated the action of dry hydrochloric and hydrobromic acid gases on ethyl oxomalonate. These substances react readily at a low temperature, giving colorless, crystallin products. This keto ester differs from the methyl ester which gave well defined, but very unstable crystallin addition products of the haloid acids on the ketone double bond, thus:



in that it appears to be more reactive and to yield a mixture of the mono-, di- and trihaloid acid addition products. These are probably correctly represented by the following typical formulas:

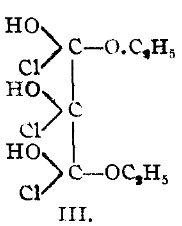


I.



II.

and



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[1] *Am. Chem. J.*, **31**, 24 (1904).

[2] See Curtiss and Spencer, THIS JOURNAL, **31**, 1054.

[3] *Ibid.*

[4] *Ibid.*, **31**, 1055.