The reaction of hydrazine hydrate with the ozonolysis product believed to be γ-butyrolactone gave a solid hydrazide, m. p. 90.5–92° (uncorr.). The mixture of this product with the hydrazide of the γ-butyrolactone prepared from ethyl succinate melted at 90.5–91.5° (uncorr.).

Dehydration of Tetrahydrofuryldi-*n*-butylcarbinol.—A mixture of 10 g. of the carbinol (III) with 0.5 g. of magnesium sulfate and 0.5 g. of potassium hydroxide was heated under a small Vigreux column. Water and an oil with an ethereal odor distilled and the residue in the flask became tarry. The experiment was repeated with similar results using lime in place of the magnesium sulfate. The combined dried products from both experiments distilled between 40 and 150° (740 mm.) with a uniform temperature rise.

Tetrahydrofuryldiphenylcarbinol with Phenylmagnesium Bromide.—To a solution of 0.6 mole of phenylmagnesium bromide in 400 ml. of ether was slowly added in small portions 48.5 g. (0.2 mole) of tetrahydrofuryldiphenylcarbinol (IV). To the reaction mixture was then added 500 ml. of dry xylene, the reflux condenser replaced by a short fractionating column with a condenser set downward for distillation and the mixture heated on an oil-bath until the vapors reached a temperature of 131°. The reflux condenser was then replaced and the xylene refluxed for fifty hours. After the reaction mixture was cooled it was poured into a mixture of cracked ice with 40 ml. of 1:1 sulfuric acid and the xylene layer separated and distilled at atmospheric pressure. Water appeared in the distillate near the end of the distillation. The residue (50 g.) solidified upon cooling and after recrystallization from petroleum ether (b. p. 60–70°) and from alcohol gave 41 g. (87%) of pure material, m. p. 107.5–108.5° (uncorr.). This melting point was unchanged when the material was mixed with a sample of V prepared by the dehydration of IV. In another experiment in which the time of refluxing was nine hours and in which the xylene was removed under reduced pressure, 76% of IV was recovered unchanged (m. p. 77–79°) along with 4 g. of an oil (b. p. 250°) which decolorized bromine in carbon tetrachloride and was apparently impure dehydration product.

Summary

Tetrahydrofuryldialkylcarbinols have been synthesized by the reaction of alkylmagnesium halides with ethyl tetrahydrofuroate and by the catalytic hydrogenation of furyldialkylcarbinols. Tetrahydrofuryldiphenylcarbinol was readily dehydrated to give 1,1-diphenyl-2,5-epoxy-1-pentene; in contrast to the dehydration of furfuryl alcohol, there was no indication of ring enlargement. The dehydration product was much more stable than 2,5-epoxy-1-pentene. Tetrahydrofuryldiphenylcarbinol was not cleaved by phenylmagnesium bromide under "forced" conditions.

ITHACA, NEW YORK RECEIVED OCTOBER 5, 1935

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF JOHNS HOPKINS UNIVERSITY]

The Preparation of Some of the Lower Alkyl Sulfonic Acids

BY D. L. VIVIAN AND E. EMMET REID

Much work has been done by earlier investigators on the preparation of alkyl sulfonic acids by various procedures, but very little effort has been made to isolate and characterize the anhydrous acids. Two exceptions occur in the work of Noller and Gordon[1] on the acids containing from nine to fourteen carbon atoms, and in that of Berthoud[2] on methyl sulfonic and ethyl sulfonic acids. The present paper gives data on the four straight-chain primary sulfonic acids containing from three to six carbon atoms.

The propyl, amyl and hexyl sulfonic acids were prepared from barium salts remaining from a previous investigation[3] by precipitating the barium with sulfuric acid. The butyl sulfonic acid was prepared by oxidation of *n*-butyl mercaptan[4] by dropping 48 g. of it into 180 cc. of concentrated nitric acid with mechanical stirring and evaporating on the steam-bath until the oxides of nitrogen were completely removed. The crude acid was diluted with ten volumes of water, neutralized with lead carbonate, filtered and the filtrate evaporated to dryness. The crude lead salt obtained in 72–96% yields was recrystallized from 80% alcohol and then decomposed in aqueous solution with hydrogen sulfide. After removing the lead sulfide the aqueous solution was concentrated on the steam-bath.

The pure anhydrous sulfonic acids were obtained from the concentrated aqueous solutions as colorless liquids after four or five distillations at 1 mm. Their hot vapors attack rubber but a coating of sodium silicate on the stoppers prevents this. The pure acids soon darken even in a vacuum.

The average purity of these acids as determined by two concordant titrations with methyl orange

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[1] Noller and Gordon, THIS JOURNAL, **55**, 1090 (1933).

[2] Berthoud, *Helv. Chim. Acta*, **12**, 859 (1929).

[3] Wagner and Reid, THIS JOURNAL, **53**, 3407 (1931).

[4] This acid was also prepared by converting butyl mercaptan into disulfide (b. p. 107–109° at 12 mm.) and oxidizing this with nitric acid, but the yield was not quite as good.

TABLE I

PROPERTIES OF THE ALKYL SULFONIC ACIDS

Acid	B. p. Temp., °C.	B. p. Pressure, mm.	M. p., °C.	Density$^{25}_{4}$
Methyl sulfonic[2]	167	10	+20	1.4844
Ethyl sulfonic[2]	...	..	−17	1.3341
n-Propyl sulfonic	136	1	+ 7.5	1.2516
n-Butyl sulfonic	147	0.5	−15.2	1.1906[a]
n-Amyl sulfonic	163	1	+15.9	1.1226
n-Hexyl sulfonic	174	1	+16.1	1.1047

[a] d^0_4 1.2117.

as indicator was as follows: propyl, 99.2; butyl, 100; amyl, 100; hexyl, 99.8%. Presumably the propyl acid still retained a trace of moisture.

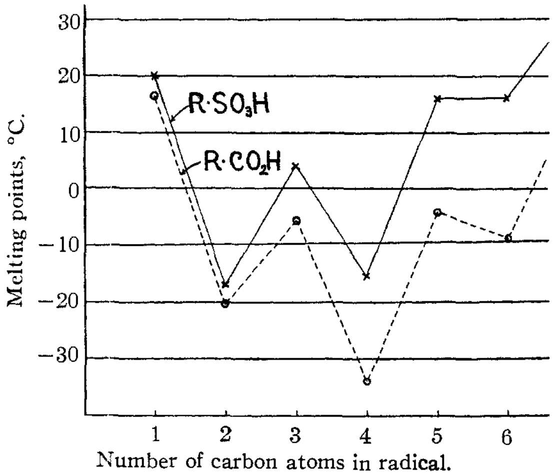

Fig. 1.—Melting points of sulfonic and carbonic acids.

The physical data obtained with these acids, together with the corresponding data for methyl and ethyl acids, are given in Table I.

These melting points are plotted along with those of the carboxy acids containing the same radicals in Fig. 1. The alternation is remarkably alike in the two series.

The acid chloride of the butyl sulfonic acid was prepared by the action of phosphorus pentachloride on the potassium salt. It boiled at 90° at 11 mm.,[5] and had d^{25}_4 1.2140, and d^0_4 1.2404.

It was thought that butyl sulfonic acid might resemble sulfuric acid in substitution reactions, but it did not react with benzene at 80°. Aniline sulfate rearranges to sulfanilic acid, but the aniline salt of butyl sulfonic acid did not undergo any change when heated several hours at 130°. This salt is readily made by adding aniline to the acid and warming slightly. After one recrystallization it melted at 162°. Gilman and Morris[6] give m. p. 159° for this salt obtained by the reaction of thionylaniline with butylmagnesium bromide.

Summary

n-Propyl, *n*-butyl, *n*-amyl and *n*-hexyl sulfonic acids have been prepared and characterized.

(5) Von Braun and Weissbach, *Ber.*, **63**, 2836 (1930).

(6) Gilman and Morris, THIS JOURNAL, **48**, 2399 (1926).

BALTIMORE, MARYLAND RECEIVED OCTOBER 3, 1935

[CONTRIBUTION FROM THE DEPARTMENTS OF ANIMAL HUSBANDRY AND HOME ECONOMICS RESEARCH, FLORIDA AGRICULTURAL EXPERIMENT STATION]

The Isolation and Some Properties of an Alkaloid from *Crotalaria spectabilis* Roth[1]

BY W. M. NEAL, L. L. RUSOFF AND C. F. AHMANN

The literature relative to the toxic species of the *Crotalariae* was reviewed in another paper,[2] in which the toxicity of *C. spectabilis* Roth was established. Previously known toxic species included *C. sagittalis* L., *C. juncea* L., *C. burkeana* Benth., *C. dura* Wood and Evans, and *C. globifera* E. Mey. Still other species have been suspected. Bessey and Stalker[3] suspected the toxic principle of *C. sagittalis* to be an alkaloid. Timson[4] found the seeds of *C. juncea* to give reactions suggesting the presence of an unidentified alkaloid. In no case had a specific alkaloid been isolated from any member of the genus.

This is a report of the isolation and some of the properties of an alkaloid isolated from *C. spectabilis*. Because of the large number of species (over 600) of *Crotalaria*, several of which have proven toxic, the name *monocrotaline* is suggested for this alkaloid. Succeeding alkaloids from this genus can then be named *dicrotoline*, *tricrotaline*, etc., following Couch's[5] recommendation for the lupine alkaloids.

(1) Presented in part before the Division of Medicinal Chemistry of the American Chemical Society at the 87th Meeting of the Society, St. Petersburg, Fla., March 25 to 30, 1934.

(2) Becker, Neal, Arnold and Shealy, *J. Agr. Research*, **50**, 911 (1935).

(3) Bessey and Stalker, *Iowa Agr. Coll. Dept. Bot. Bull.*, 111 (1884).

(4) Timson, *Rhodesia Agr. J.*, **26**, 668 (1929).

(5) Couch, THIS JOURNAL, **56**, 155 (1934).