

VIII (0.2 g.) was dissolved in 8 ml. of ethanol and converted to the 2,4-dinitrophenylhydrazone by treatment with a solution of 0.16 g. of 2,4-dinitrophenylhydrazine in 0.8 ml. of sulfuric acid and 1.2 ml. of water, diluted with 4 ml. of ethanol. The mixture was heated at the reflux temperature for two hours after the appearance of a precipitate. On cooling, filtering and washing with cold alcohol a yield of 0.25 g. (88%) of the dinitrophenylhydrazone was obtained, m. p. 169–170°. After recrystallization from ethanol-ethyl acetate, acetonitrile and chloroform-carbon tetrachloride, the derivative was a crystalline crimson powder with a constant m. p. of 177–178°.

Anal. Calcd. for $C_{18}H_{16}O_4N_4$: C, 61.36; H, 4.58. Found: C, 61.34; H, 4.70.

Synthesis of Ethyl (2-Allyl-1-indanylidene)-cyanoacetate (VIIA) as a Proof of Structure.—A mixture of 2.0 g. of VIII, 1.28 g. of ethyl cyanoacetate, 0.18 g. of ammonium acetate, 0.54 g. of glacial acetic acid and 5 ml. of benzene was heated under reflux for nineteen hours, while the water formed was removed from the refluxing benzene with a small Dean and Stark type continuous separator. During the period of heating, seven additional portions of ammonium acetate (0.18 g.) and one of acetic acid (0.54 g.) were added.¹¹ The mixture was poured into 25 ml. of benzene and washed with ten 5-ml. portions of water. The benzene solution was combined with a benzene extract of the water washings, dried over magnesium sulfate and concentrated under reduced pressure. The residue crystallized on seeding, and after washing with cold pentane containing 10% of ether amounted to 0.32 g. (10%), m. p. 76–78°. An additional 0.19 g. (6%) of VIIA was obtained from the mother liquors by evaporative distillation and recrystallization. Crystallization to constant melting point from cyclohexane gave colorless needles of

(11) Based on a procedure for condensing ethyl cyanoacetate with unreactive ketones to be published later by E. J. Cragoe, Jr., Charles M. Robb and James M. Sprague.

VIIA, m. p. and mixed m. p. with the sample of VIIA obtained by rearrangement of III, 80.5–81°.

Anal. Calcd. for $C_{17}H_{17}O_2N$: C, 76.38; H, 6.41. Found: C, 76.24; H, 6.53.

Ultraviolet Absorption Spectra.—The absorption curves in Fig. 2 were obtained with solutions of IIA, III and VIIA (prepared by rearrangement of III) in 95% ethanol, using a Beckman Model DU quartz ultraviolet spectrophotometer.

Active Hydrogen Determinations.—Values for molar equivalents of active hydrogen which are cited were obtained by shaking samples of the compounds with an excess of methylmagnesium iodide in diisoamyl ether at room temperature for one hour and at 80–100° for forty minutes, and measuring the methane evolved. For VI the times were thirty minutes at room temperature and twenty minutes at 80–100°.

Summary

Ethyl (3-indenyl)-allylcynoacetate (III) has been prepared by the alkylation of ethyl (1-indanylidene)-cyanoacetate (IIA). The skeletal structure of III has been confirmed by reduction and hydrolysis to (1-indanyl)-propylacetic acid which was synthesized by an independent method. Rearrangement of III was observed to occur at 125°, with migration of the allyl group to give ethyl (2-allyl-1-indanylidene)-cyanoacetate (VIIA), the skeletal structure of which was established by an independent synthesis. Evidence supporting the structure of III and indicating the position of the double bonds in IIA and VIIA was obtained from their ultraviolet absorption spectra.

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[CONTRIBUTION FROM NORTH DAKOTA STATE COLLEGE, FARGO, N. D., AND LEHIGH UNIVERSITY, BETHLEHEM, PENNA.]

Dibenzofuran-2-sulfonic Acid. I. The Free Acid and its Alkali Salts

BY RAY WENDLAND AND CHARLES H. SMITH, WITH RAFFAELE MURACA

Dibenzofuran-2-sulfonic acid has been prepared in this Laboratory as a pure compound, this being apparently its first indubitable preparation. The compound is a strong acid which possesses the advantageous property, unusual for sulfonic acids, of being easily crystallizable from cold water. Contrary to reports¹ it is not particularly hygroscopic and can be vacuum dried to a composition exhibiting a neutral equivalent of 249 ± 1 (theor., 248.25). This preparation melts sharply at 147.0 to 147.5°.

Earlier studies of dibenzofuran sulfonic acids are those of Zehenter,¹ Gilman and co-workers,^{2,3,4} and Hoffmeister.⁵ Zehenter obtained a product closely approximating the monosulfonic acid in composition by the action of fuming sulfuric acid on 2,2'-dihydroxydiphenyl, but his acid melted

variously over the range 115 to 165°. Gilman's studies produced compounds with the following orientations: 2-sulfo,² 2,8-disulfo by the method of Hoffmeister,⁵ 4,6-disulfo,³ and 3-sulfo.⁴

This important work is meritorious for having determined the orientation influences within the ring system. However, since we have a free sulfonic acid of sharp melting point, there is a question whether Gilman and co-workers prepared their sulfonation products as free sulfonic acids in view of the physical constants presented. The following summary of their work should be examined:

(a) The 2-sulfonic acid was supposedly isolated by acidification of a solution of the sodium salt. The decomposition of the product above 300° without melting implied only the metal salt present; (b) the 4,6-disulfonic acid was prepared by oxidation of the sulfinic acid with potassium permanganate, whereby the potassium salt must have been formed. The product isolated showed only decomposition at 300° with no melting, implying again a metal salt; (c) the 3-sulfonic acid

(1) J. Zehenter, *J. prakt. Chem.*, **131**, 331 (1931).

(2) H. Gilman, E. W. Smith and H. J. Oatfield, *THIS JOURNAL*, **56**, 1412 (1934).

(3) H. Gilman and R. V. Young, *ibid.*, **57**, 1121 (1935).

(4) H. Gilman, E. W. Smith and Lee Cheney, *ibid.*, **57**, 2095 (1935).

(5) W. Hoffmeister, *Ann.*, **159**, 211 (1871).

was made from the sulfinic acid by the same process as in (b), and the product (K salt ?) decomposed at high temperature without melting.

The above comment has been made particularly to show that the isolation of many free sulfonic acids is attended by special difficulties, and that satisfaction is not altogether common.

It has been observed here that dibenzofuran-2-sulfonic acid, I, can be conveniently prepared by the direct sulfonation of dibenzofuran using concentrated sulfuric acid at 100°. Inevitably the reaction yields some of the much more soluble disulfonic acid. However, the desired monosulfonic acid can be obtained simply by chilling the diluted sulfonation mixture which leads to rapid crystallization of the free acid in large shimmering platelets. Furthermore, the sodium salt of this acid and likewise its potassium salt show extremely low solubilities in water—facts which have not previously been exploited.

The present investigation has therefore been aimed at determining three results: (1) the course of the sulfonation reaction of dibenzofuran, *i. e.*, the amounts of mono and disulfonic acids formed by action of sulfuric acid at 100°, (2) the properties of the mono acid, and (3) the quan-

titative solubilities of various salts of the mono acid.

Experimental

1. **Sulfuric Acid Sulfonation of Dibenzofuran and Isolation of the Monosulfonic Acid.**—The quality of the sulfonic acid was somewhat influenced by the source of the dibenzofuran. The Reilly Tar and Chemical Company product once crystallized from alcohol gave excellent results. The standard procedure for sulfonation employed throughout the work was as follows: Concentrated sulfuric acid and dibenzofuran were mixed together in the amounts of 2.4 moles to 1.0 and agitated by means of a sealed stirrer in a steam-bath for various times from one to four hours. The free monosulfonic acid precipitated after the sulfonation mixture was poured into twice its volume of water and chilled. Residual monosulfonic acid was precipitated as the sodium salt by neutralization. Barium chloride was added to the filtrate to precipitate both unreacted sulfuric acid and dibenzofuran disulfonic acid. The latter was separated from barium sulfate by virtue of its solubility in boiling water.

The isolation of these products showed that the sulfonation varied with time according to Table I.

TABLE I

DIBENZOFURAN OCCURRING AS MONO AND DISULFONIC ACIDS AFTER SULFONATION WITH 2.4 MOLES OF SULFURIC ACID AT 100°

Reaction time, hr.	Monosulfonic acid, %	Disulfonic acid, %	Percentage original H ₂ SO ₄ remaining
1	75	17	37
2	54	28	35
3	52	29	32
4	..	42	..

^a Expressed as mole per cent. of dibenzofuran used.

It is obvious from Table I that some dibenzofuran remains unaccounted for, although it had reacted completely with the sulfuric acid, even during one hour. The remainder probably was converted to poly-sulfonation products of unusual solubility which could not be isolated by the procedure employed. The best yield of the monosulfonic acid was obtained after *one* hour of sulfonation, hence this period was chosen for the quantitative production of the acid. A shorter reaction period left some of the dibenzofuran unreacted. Likewise a decrease in the molar ratio of sulfuric acid/aromatic gave a lower yield of the sulfonic acid and left behind unreacted dibenzofuran.

2. Properties of Dibenzofuran-2-sulfonic Acid

(a) **Identity.**—The acid isolated in Section 1 is the 2-sulfonic acid. Proof was established by comparison with the authentic 2-acid obtained by use of chlorosulfonic acid on dibenzofuran.² This preparation was repeated here, and the free sulfonic acid crystallized directly from the sulfonation mixture, instead of being precipitated as the sodium salt according to the Gilman procedure. Both acids (after twenty-four hours of drying over sulfuric acid) showed melting points of 147 ± 0.5°, and a mixed melting point determination showed no depression. Aniline salts of the two were prepared, and found to melt at 259 ± 0.5°. The theoretical neutral equivalent of the monosulfonic acid is 248.25; that obtained by Gilman's procedure gave 254; ours gave 248.6. *Anal.* Calcd.: S, 12.91; Found: S, 12.40.

(b) **Acidity Characteristics.**—Conductivity measurements revealed the properties of a strong acid. The data indicate that the equivalent conductance at infinite dilution is of the order of 350–400. It therefore compares with the nitro halobenzenesulfonic acids measured by Elgersma,⁶ who found these to have an equivalent con-

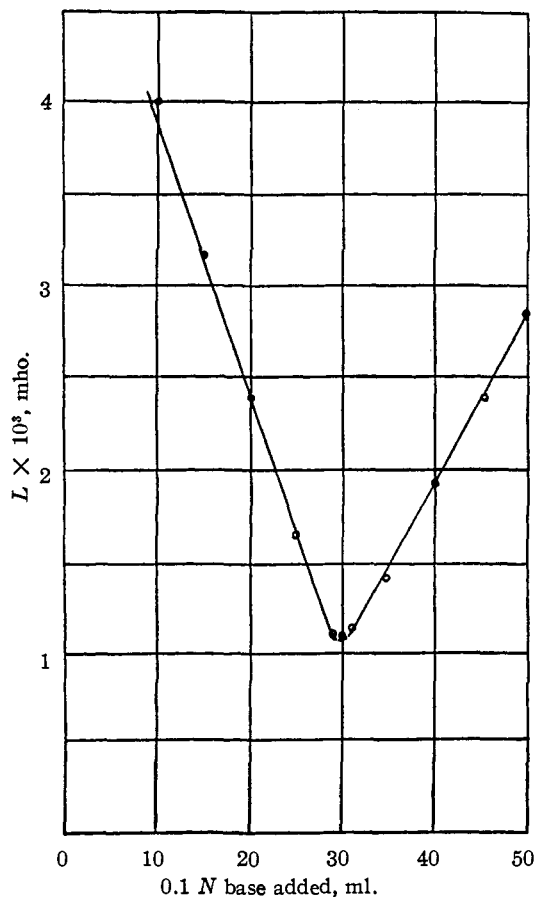


Fig. 1.—Conductimetric titration of DBF-2-S with sodium hydroxide.

(6) J. N. Elgersma, *Rec. trav. chim.*, **48**, 770 (1929).

ductance of 377 (cm.²/ohm equivalent). Table II summarizes our findings.

TABLE II

CONDUCTANCE OF DIBENZOFURAN-2-SULFONIC ACID AT 25°

Equivs./liter	Specific conductance $\times 10^3$ (ohm ⁻¹ × cm. ⁻¹)	Equivalent conductance (cm. ² /ohm equiv.)
0.020	5.9	290
.010	3.4	340
.005	1.8	370
.0025	0.88	350
.0012	.48	400
.00062	.23	380

The pH of a 0.20 *N* (5%) solution of the sulfonic acid was determined and found to be 0.80. A corresponding hydrogen ion activity of 0.2 of unity would give a pH of 0.7. The calculated dissociation of the acid at 0.2 *N* = $(10^{-0.8}/10^{-0.7})100 = 79\%$.

(c) **Solubility.**—The water solubility of the sulfonic acid was determined at 0 and 25°. Concentrated solutions of the acid were prepared at 50–60°, then chilled in tall cylinders for twenty-four hours. Titration of the clear liquid above the precipitated acid gave the following results: solubility at 25° = 0.34 *N* = 8.5 g./100 ml.; at 0° = 0.0887 *N* = 2.2 g./100 ml.

3. **Precipitation of Sodium and Potassium, and Various Other Cations by Dibenzofuran-2-sulfonic Acid.**—The recrystallized acid was dissolved in water at various concentrations ranging downward from 2.0%. Such solutions were neutralized by the addition of sodium, potassium, ammonium and barium hydroxides, after which the resulting solutions were diluted to a standard volume and chilled in ice. The appearance of a precipitate immediately indicated the point at which saturation had been reached. By determining the amount of precipitated salt, and knowledge of the original amount produced, one can calculate the solubilities of these salts. The solubility of the lithium salt was determined by addition of the acid to dilute lithium chloride solutions.

A great many other metal ions were precipitated from their dilute aqueous solutions by addition of the 2-sulfonic acid. The results of these various determinations are summarized in Tables III and IV.

TABLE III

SOLUBILITIES OF VARIOUS SALTS OF DIBENZOFURAN-SULFONIC ACID AT 0°

Cation	Solubility (g./100 ml.)	Solubility product
Na	0.300	1.23×10^{-4}
K	0.520	3.31×10^{-4}
Ba	0.094	1.29×10^{-8}
Li	0.74	8.5×10^{-4}
NH ₄	1.87	49.7×10^{-4}

Ag, Cu⁺, Hg⁺, Mg, Ca, Zn, Al, Pb⁺, Sb⁺, Bi⁺, Cr⁺, Mn⁺, Ni, Fe⁺, Co⁺-chloride and sulfate salt solutions of all these metals in 1% concentration, gave abundant precipitation when the acid solution was added.

TABLE IV

ANALYSIS OF SODIUM, POTASSIUM, AND BARIUM SALTS OF DIBENZOFURAN-2-SULFONIC ACID (DRIED IN VACUUM OVEN TWO HOURS AT 110°)

Salt	Molecular formula	Per cent. sulfur Calcd.	Per cent. sulfur Found	Per cent. metal Calcd.	Per cent. metal Found
Na	(C ₁₂ H ₇ SO ₄)Na	11.85	11.76	8.51	8.19
K	(C ₁₂ H ₇ SO ₄)K	11.20	11.05	13.63	13.27
Ba	(C ₁₂ H ₇ SO ₄) ₂ Ba	10.15	10.10	21.75	21.34

The sodium and potassium salts were analyzed by combustion in a platinum crucible with sulfuric acid to form metal sulfates.

The very low water-solubility of the sodium, potassium, and lithium salts is noteworthy—a phenomenon that augurs a new technique in the determination of these metals.

Summary

Dibenzofuran-2-sulfonic acid has been prepared and crystallized from water. The acid appears to be a general metal ion precipitant, even for lithium, sodium and potassium, and for these metals offers promise as an analytical reagent.

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(7) Original manuscript received June 1, 1948.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF DUKE UNIVERSITY]

Base Catalyzed Polymerization of Styrene

BY JAMES J. SANDERSON¹ AND CHARLES R. HAUSER

A study of the base catalyzed polymerization of styrene has been in progress in this Laboratory for some time. In view of the recent paper by Beaman² on the base catalyzed polymerization of methacrylonitrile it seems desirable to publish our results.

We have found that styrene is polymerized by sodium amide in liquid ammonia to give an easily pulverized white solid, melting at 130–170°, and having an average molecular weight of about 3000. On fusion this polymer is transformed to a brittle, glassy solid. The properties of this material are those reported for polystyrene of the same average molecular weight prepared by heating styrene

at 240°.³ Results obtained under varying conditions are summarized in Table I. It can be seen that the yields and average molecular weights are approximately the same using 5, 10 and 100 mole

TABLE I

POLYMERIZATION OF STYRENE BY SODIUM AMIDE IN LIQUID AMMONIA

Mole % of NaNH ₂	Reaction time, min.	Yield, %	Average mol. weight
5	240	71	2900
10	240	72	3200
100	240	68	3100
100	120	64	..
100	20	40	4300

(1) Carbide and Carbon Chemicals Corporation Fellow, 1946–1948.

(2) Beaman, *THIS JOURNAL*, **70**, 3115 (1948).

(3) Staudinger, Brunner, Frey, Garbsch, Signer and Wehrli, *Ber.*, **62**, 241 (1929).