

ternal fields, is of order unity, the molecular polarization per  $-\text{CH}_2\text{CHCl}-$  group is 30 cc., because

$$p = \frac{E \epsilon' - 1}{F} \quad (9)$$

This corresponds to a moment equal to  $1.2 \times 10^{-18}$ , which compares favorably with the values found for Cl-dipoles in simple molecules, where liquid friction is the only restraint on molecular rotation.

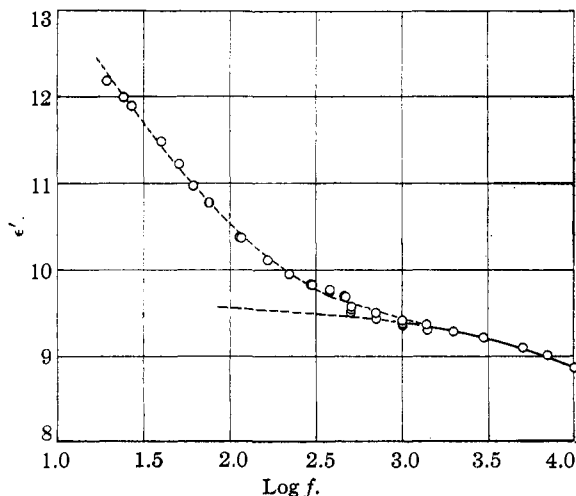


Fig. 10.—Polarization capacitance.

Two other interesting facts are contained in the data. The first is the sudden increase (Fig. 10) with decreasing frequency of the dielectric con-

stant of the 35 polyvinyl chloride–65 tricresyl phosphate sample. This may be due to polarization capacity acting at the electrodes; more data are needed to decide the question. The second is the corresponding rise in loss factor for this sample. If these two properties really are volume properties and not surface effects, the system polyvinyl chloride–tricresyl phosphate has two dispersion regions. The region from the gel stage through the viscous solutions to dilute solutions of polymers in plasticizer needs considerable more investigation, which must be prefaced by a study of experimental methods for handling these materials.

### Summary

1. Dielectric constants and loss factors at  $40^\circ$  and 20 cycles to 10 kilocycles under low voltage are reported for the system polyvinyl chloride–tricresyl phosphate, over the entire concentration range.

2. As a function of composition, the maximum absorption and the dielectric dispersion appear in the range 70–50% polymer, where the macroscopic viscosity has its most rapid rate of change with composition.

3. A characteristic difference between free dipoles and dipolar polymers is pointed out: the former can assume a normal distribution of orientations, while the latter have a distribution determined by the chain orientation.

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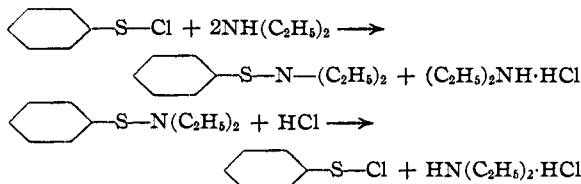
RECEIVED JUNE 3, 1939

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

## The Use of *o*-Nitrobenzenesulfonyl Chloride in the Identification of Amines

By JOHN H. BILLMAN AND EUGENE O'MAHONY

It has been reported by Zincke<sup>1</sup> and Lecher<sup>2</sup> that amines would react with aromatic sulfonyl chlorides to produce amides of sulfenic acid which upon treatment with hydrochloric acid could be hydrolyzed. In certain cases, solid amides were obtained.



(1) T. Zincke and F. Farr, *Ann.*, **391**, 57–88 (1912).

(2) H. Lecher and F. Holtschneider, *Ber.*, **57**, 755–758 (1924).

The purpose of our work was to investigate further these reactions using substituted benzenesulfonyl chlorides in an attempt to produce suitable solid derivatives of amines for means of identification and to examine the ease of hydrolysis of the amides back to the amines.

It was found that *o*-nitrobenzenesulfonyl chloride was quite satisfactory as a reagent. The compound is easily prepared and does not react readily with water or alcohol, thereby affording the identification of amines in water solution.

The reactions between reagent and amines were carried out in ether solution and in all cases took place spontaneously. However, no reaction could

be obtained when *o*-nitrobenzenesulfonyl chloride was treated with *o*-nitroaniline or diphenylamine. All of the derivatives were insoluble in 10% alkali.

derivatives of tertiary amines and higher melting amides of the aliphatic amines.

### Experimental

The *o*-nitrobenzenesulfonyl chloride was prepared from *o,o'*-dinitrodiphenyl disulfide and chlorine by the method described in "Organic Syntheses."<sup>3</sup>

The amides described in this paper were all prepared by the addition of an ether solution of *o*-nitrobenzenesulfonyl chloride to an ether solution of the amine. When an aqueous solution of the amine, as dilute as 25%, was used, enough ether was added to produce a homogeneous solution before treatment. The amount of reagent required for the reaction was determined by slowly adding the sulfonyl chloride and observing whether or not further precipitation of the hydrochloride occurred. The hydrochloride formed was filtered and washed thoroughly with dry ether. The filtrates were collected and the ether evaporated off. The remaining material was easily solidified and recrystallized from 95% alcohol.

The hydrolysis of the amides was accomplished by dissolving the amide in a slight excess of dry ether and passing in dry hydrogen chloride. At the end of three minutes the gas was turned off and the solution filtered. The insoluble amine hydrochloride was then washed with dry ether and weighed. To recover the amine, sodium hydroxide was added to the hydrochloride.

### Summary

1. *o*-Nitrobenzenesulfonyl chloride has been found to form a large number of solid derivatives of amines.
2. The reaction goes quickly and gives sharp melting compounds.
3. The amide derivatives are readily hydrolyzed to the amine hydrochloride in three minutes.
4. Anhydrous and aqueous amines were both used in the experiment without difficulty.

TABLE I  
PROPERTIES OF AMINE DERIVATIVES

Amine	M. p. <sup>a</sup> of amide, °C.	M. p. of hydrochloride, °C.	Analyses of amide, %	
			Calcd.	Found
Ammonia <sup>2</sup>	124-125 dec.	350 dec.		
Aniline <sup>b</sup>	88.5-89	198	S, 13.00	12.95
<i>p</i> -Anisidine	138-138.5	220 dec.	N, 10.00	10.15
<i>p</i> -Bromoaniline	146-146.5	Dec.	N, 8.62	8.73
<i>n</i> -Butylamine	27-28	142-142.5	S, 14.16	14.00
<i>p</i> -Chloroaniline	143.5-144	194 dec.	N, 9.98	10.01
Cyclohexylamine	51.5-52	206-207	N, 11.12	11.09
Diethylamine	Oil	215-223		
Dimethylamine	62.5-63	171	N, 14.14	13.93
Ethylamine	32.5-33	108	S, 16.15	15.92
Methylamine	35.5-36	225-226	S, 17.38	17.11
<i>N</i> -Methylaniline	86-86.5	121-122	N, 10.78	10.85
$\alpha$ -Naphthylamine <sup>c</sup>	130.5-131	260 dec.	N, 9.46	9.30
$\beta$ -Naphthylamine <sup>b</sup>	202-202.5	254	N, 9.46	9.33
<i>n</i> -Propylamine	Oil	157-158		
<i>o</i> -Toluidine	115.5-116	215	S, 12.31	12.20
<i>m</i> -Toluidine	106.5-107	228	N, 10.77	10.90
<i>p</i> -Toluidine	136-136.5	243	N, 10.77	10.86

<sup>a</sup> Melting points are corrected. <sup>b</sup> Melting points differ from those previously reported in the literature. <sup>c</sup> Softens at 125°.

These solid amides of *o*-nitrobenzenesulfenic acid, when dissolved in ether and treated with gaseous hydrogen chloride, for three minutes, regenerated the sulfonyl chloride and gave an approximately quantitative recovery of the amine in the form of its hydrochloride.

TABLE II  
AMIDES HYDROLYZED

Amide of	% recovery of amine hydrochloride
Cyclohexylamine	98.5
<i>m</i> -Toluidine	95.0
Dimethylamine	97.4
Aniline	98.7

Further experiments are being carried out using other sulfonyl chlorides in an attempt to obtain

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RECEIVED MAY 10, 1939

(3) *Org. Syntheses*, **15**, 45 (1935).