

disilane in 100 ml. of ether. The ether was distilled and the resulting paste was heated at about 50° for 3 hr. Color Test I was then negative. Petroleum ether (b.p. 60–70°) was added. Filtration gave a clear solution which on cooling deposited an oil. After stripping off the petroleum ether, distillation of the residue gave three main fractions.

The first, b.p. 169–180° (20 mm.), 3.24 g. (7.6%), was redistilled at 15 mm. and boiled at 165–167°. The infrared spectrum of this oil was identical with that of an authentic specimen of dichlorodiphenylsilane. Further confirmation that the product was dichlorodiphenylsilane was obtained by treatment of 1.22 g. of the chlorosilane with *p*-biphenyllithium. There was obtained 1.86 g. (81%) of di-*p*-biphenyldiphenylsilane, m.p. 169–171° (reported¹⁹ 169–170°). A mixed melting point with an authentic specimen of di-*p*-biphenyldiphenylsilane was not depressed.

A second fraction distilled over the range 229–240° (20 mm.) and weighed 3.45 g. This was recrystallized from petroleum ether (b.p. 60–70°) and melted partially at 97°, indicative of the possible presence of chlorotriphenylsilane. Distillation of this solid gave no pure products.

A third fraction distilled over the range 185–215° (0.3 mm.), 7.1 g., and crystallized on standing. Recrystallization from petroleum ether (b.p. 60–70°) gave 3.5 g., melting at 125–128° (partial). Several recrystallizations did not sharpen the melting point. One g. of this material was treated with excess methyllithium. Hydrolysis, followed by work-up in the usual way, gave some solid, m.p. 133–143°. This was dissolved in hot petroleum ether (b.p. 60–70°) and chromatographed on an alumina column to give 0.3 g. of solid, m.p. 140–142° (cloudy). A mixed melting point with 1,2-dimethyl-1,1,2,2-tetraphenyldisilane was not depressed.

A small amount of tetraphenylsilane was scraped from the condenser walls after the distillation and recrystallized from benzene, m.p. 236°.

The distillation residue consisted of a large amount of brown polymer which, though insoluble in most common solvents, dissolved slowly in benzene.

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CHEMICAL LABORATORY
IOWA STATE COLLEGE
AMES, IOWA

(19) L. Spialter, D. C. Priest, and C. W. Harris, *J. Am. Chem. Soc.*, **77**, 6227 (1955).

Magnesium Salts of Aromatic Arsonic Acids. The Nitration of Benzenearsonic Acid

LEON D. FREEDMAN AND G. O. DOAK

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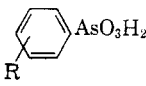
Magnesium salts of most phosphonic acids are soluble at room temperature but are precipitated on heating.¹ However, arylphosphonic acids con-

(1) L. D. Freedman and G. O. Doak, *J. Am. Chem. Soc.*, **77**, 6221 (1955); see also *Chem. Revs.*, **57**, 479 (1957).

taining bulky *ortho* substituents do not form insoluble magnesium salts either at room temperature or when heated. This fact permitted the isolation of *o*-nitrophenylphosphonic acid from the mixture of isomers obtained by nitrating phenylphosphonic acid.¹ It has been known for over half a century that the magnesium salts of arsonic acids are more soluble in cold water than in hot.² And, indeed, the fact that atoxyl³ yields a precipitate with magnesia mixture only upon boiling was cited by Ehrlich and Berthelm⁴ as evidence that atoxyl is an arsonic acid derivative. However, a survey of the literature revealed very little information concerning the effect of the substituents on the solubility of magnesium salts of aromatic arsonic acids.⁵ Since we had available in this laboratory a number of aromatic arsonic acids, it was of interest to determine whether the generalizations previously noted¹ for arylphosphonic acids were also valid for the analogous arsonic acids.

A sample of each arsonic acid listed in Table I was dissolved in dilute aqueous ammonia and treated with magnesia mixture exactly as described for the phosphonic acids.¹ The following results were obtained: (1) Only one arsonic acid (*N*-*p*-toluylarsanilic acid) gave an insoluble magnesium salt at room temperature. (2) *o*-Toluenearsonic and *o*-bromobenzenearsonic acids gave sparse precipitates on heating; all other compounds

TABLE I
ARSONIC ACIDS STUDIED

	
R =	
H	<i>p</i> -NHCOCH ₃
<i>o</i> -, <i>m</i> -, <i>p</i> -NO ₂	<i>p</i> -AsO ₃ H ₂
<i>o</i> -, <i>m</i> -, <i>p</i> -Cl	<i>p</i> -NHCH ₂ COOCH ₃
<i>o</i> -, <i>p</i> -Br	<i>p</i> -NHCOC ₆ H ₄ CH ₃ - <i>p</i> '
<i>o</i> -, <i>p</i> -CH ₃	2-NO ₂ -6-CH ₃
<i>m</i> -, <i>p</i> -SO ₂ NH ₂	2-NO ₂ -3-COOH
<i>m</i> -COOH	3-NO ₂ -4-NH ₂
<i>p</i> -COOCH ₃	3-NO ₂ -4-OH
<i>o</i> -C ₆ H ₅	3-NO ₂ -4-COOH
<i>p</i> -NH ₂	3-NH ₂ -4-(CH ₂) ₃ COOH
<i>p</i> -OH	

(2) W. M. Dehn, *Am. Chem. J.*, **33**, 101 (1905).

(3) "Atoxyl" is a trivial name for the sodium salt of arsanilic acid. It was first prepared by A. Bechamp, *Compt. rend.*, **56**, 1172 (1863), and was originally believed to be an anilide of arsenic acid.

(4) P. Ehrlich and A. Berthelm, *Ber.*, **40**, 3292 (1907).

(5) L. Benda, *J. prakt. Chem.*, **95**, 75 (1917), reported that several anthraquinonearsonic acids yield precipitates with magnesia mixture in the cold. H. Schmidt, *Ann.*, **421**, 159 (1920), found that *o*-nitrobenzenearsonic acid does not give any precipitate on boiling with magnesia mixture, the magnesium salt separating only on prolonged standing at room temperature. G. O. Doak, H. Eagle, and H. G. Steinman, *J. Am. Chem. Soc.*, **64**, 1064 (1942), state that certain diarsonic acids give insoluble magnesium salts in the cold, whereas the magnesium salts of monoarsonic acids usually precipitate only on heating.

containing *ortho* substituents did not form insoluble magnesium salts. (3) With three exceptions, compounds lacking *ortho* substituents gave copious precipitates on heating. The exceptions, *m*-carboxybenzenearsonic acid, *m*-sulfamylbenzenearsonic acid and (2-amino-4-arsenophenyl)butyric acid, failed to give precipitates with magnesia mixtures. It is probably significant that the exceptions are acid substituted benzenearsonic acids.

The above results are similar to those previously obtained with arylphosphonic acids. In both types of acids the presence of *ortho* substituents seems to inhibit the formation of insoluble magnesium salts. This effect may often be useful in separating *ortho* isomers from mixtures of isomeric acids. In the work described below, the magnesium salt technique was used in the investigation of the products formed in the nitration of benzenearsonic acid.

The Nitration of Benzenearsonic Acid. Michaelis and Lösner⁶ were the first to attempt the nitration of benzenearsonic acid. They found that it was unaffected by fuming nitric acid even at 100° but that it could be nitrated with 100% nitric acid. The nitrobenzenearsonic acid obtained was believed to be a single isomer, but no information about the position of the nitro group was obtained. The constitution of the acid was established by Bertheim and Benda,⁷ who showed that it is *m*-nitrobenzenearsonic acid. Isomeric compounds could not be detected in the reaction mixture.

We confirmed the observation of Michaelis and Lösner that benzenearsonic acid is remarkably difficult to nitrate. Although phenylphosphonic acid can be nitrated at room temperature with fuming nitric acid to give a virtually quantitative yield of mononitrated phenylphosphonic acid, this procedure is without effect on benzenearsonic acid. The use of anhydrous nitric acid at the boiling point was, however, quite satisfactory. From the reaction mixture an 83% yield of a nitrobenzenearsonic acid was obtained. This material was shown to be pure *m*-nitrobenzenearsonic acid by comparison with an authentic sample prepared from *m*-nitrobenzenediazonium fluoroborate.⁸ Using the magnesium salt procedure, we isolated also a small yield (1.6%) of a different nitrobenzenearsonic acid, which was shown to be the pure *o*-isomer by comparison with a commercial sample (Eastman Kodak White Label). It is clear, then, that the nitration of benzenearsonic acid does not yield only a single product.

The fact that benzenearsonic acid is much more difficult to nitrate than phenylphosphonic acid requires explanation. A possible reason may be associated with a difference in the base strengths of the two acids, *i.e.*, the relative ease with which they

are protonated. Although the appropriate dissociation constants have not been reported, the *acid* dissociation constants of benzenearsonic⁹ and phenylphosphonic¹⁰ acids are well-known. And if we assume that the acid dissociation constants of the species $C_6H_5MO_3H_3^+$ (where M is either P or As) are in the ratio $1:10^{-5}:10^{-10}$, then the first pK_a of $C_6H_5AsO_3H_3^+$ is about -1 , while the first pK_a of $C_6H_5PO_3H_3^+$ is about -3 .¹¹ The acidity function (H_0) of fuming nitric acid has not been determined, but it seems probable that benzenearsonic acid is almost completely protonated in this solvent because the acidity function of 9.5 M nitric acid is -2 .¹² The difficulty in nitrating benzenearsonic acid is caused, then, by the deactivating effect of the positively charged arsono group. We can not be sure as to what extent phenylphosphonic acid is protonated in fuming nitric acid, but it is possible that the phosphonic acid exists to a considerable degree in this solvent as an uncharged molecule, which we would expect to be readily nitrated.

EXPERIMENTAL¹³

The nitration of benzenearsonic acid. Benzenearsonic acid (50 g.) was nitrated with 270 ml. of anhydrous nitric acid (Baker and Adamson) under conditions similar to those described in ref. 6. The reaction mixture was diluted with 375 ml. of water and cooled, whereupon 45.9 g. of pure *m*-nitrobenzenearsonic acid, m.p. 177–180°, crystallized from solution. A second crop (4.9 g.) of *m*-nitrobenzenearsonic acid was obtained by evaporating the mother liquor to incipient crystallization. Both crops were identified by analysis, by mixed m.p. with an authentic sample and by ultraviolet absorption ($\lambda_{max} = 252.5 m\mu$, $\epsilon_{max} = 7,800$).

The filtrate from the second crop of *m*-nitrobenzenearsonic acid was evaporated to dryness, and the residue was dissolved in 50 ml. of 10% aqueous ammonia. When the resulting solution was mixed with 200 ml. of 0.27M magnesium chloride solution, a precipitate formed immediately. This precipitate must consist of a magnesium salt of inorganic arsenic acid, as neither benzenearsonic acid nor the isomeric nitrobenzenearsonic acids give insoluble magnesium salts in the cold. The precipitate, after being washed with 3% aqueous ammonia and dried at 100° for an hour, weighed 2.56 g. and contained 34.9% arsenic. This result indicates that about 5% of the benzenearsonic acid used had been converted to inorganic arsenic during the course of the nitration.

The filtrate and washings from the magnesium arsenate were combined and boiled to precipitate the magnesium salt

(9) D. Pressman and D. H. Brown, *J. Am. Chem. Soc.*, **65**, 540 (1943), report for $C_6H_5AsO_3H_2$, $K_1 = 3.4 \times 10^{-4}$, $K_2 = 3.3 \times 10^{-9}$.

(10) H. H. Jaffé, L. D. Freedman, and G. O. Doak, *J. Am. Chem. Soc.*, **75**, 2209 (1953), report for $C_6H_5PO_3H_2$, $pK_1 = 1.83$, $pK_2 = 7.07$.

(11) L. Pauling, *General Chemistry*, W. H. Freeman and Co., San Francisco, Calif., 1954, p. 453.

(12) L. P. Hammett and M. A. Paul, *J. Am. Chem. Soc.*, **56**, 827 (1934).

(13) Melting points were determined by the method of J. F. Morgan and C. S. Hamilton, *J. Am. Chem. Soc.*, **66**, 874 (1944). The ultraviolet absorption spectra were determined in 95% ethanol according to the procedure described by H. H. Jaffé and L. D. Freedman, *J. Am. Chem. Soc.*, **74**, 1069 (1952).

(6) A. Michaelis and H. Lösner, *Ber.*, **27**, 263 (1894).

(7) A. Bertheim and L. Benda, *Ber.*, **44**, 3297 (1911).

(8) G. O. Doak and L. D. Freedman, *J. Am. Chem. Soc.*, **73**, 5656 (1951).

of any *m*-nitrobenzenearsonic acid still remaining in solution. The precipitate, after being washed with hot water and dried *in vacuo* over sulfuric acid, weighed 3.94 g. It was not further investigated.

The filtrate from the above precipitate was evaporated to dryness, and the residue was dissolved in 500 ml. of water and treated with 160 g. of Dowex-50 (hydrogen ion form). The resin was removed, and the resulting solution evaporated to dryness. Recrystallization of the residue from water yielded 1.0 g. of pure *o*-nitrobenzenearsonic acid, m.p. 225–229°. This was identified by analysis, by mixed m.p. with an authentic sample, and by ultraviolet absorption ($\lambda_{\max} = 262 \text{ m}\mu$, $\epsilon_{\max} = 5740$).

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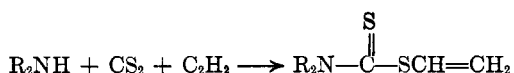
VENEREAL DISEASE EXPERIMENTAL LABORATORY
COMMUNICABLE DISEASE CENTER
U. S. PUBLIC HEALTH SERVICE
SCHOOL OF PUBLIC HEALTH
UNIVERSITY OF NORTH CAROLINA
CHAPEL HILL, NORTH CAROLINA

Synthesis of Vinyl *N,N*-Dialkyldithiocarbamates

J. C. SAUER

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Saturated esters of dithiocarbamic acids are well known, generally being prepared by the reaction of an amine, carbon disulfide, and an alkyl halide.¹ Vinyl esters of the dithiocarbamic acids have not been reported. Now it has been found that vinyl *N,N*-dialkyldithiocarbamates can be readily prepared by the interaction of a dialkylamine, carbon disulfide, and acetylene. The vinylations were car-



ried out at applied acetylene pressures of 13–18 atm. and a temperature of 130°. Tetrahydrofuran was the best solvent investigated, being superior to dimethylformamide or water. Catalytic amounts of potassium hydroxide gave slightly improved yields of product, but the catalyst was not otherwise essential. Yields of vinyl esters ranged from 52 to 60%.

The characterization of these new vinyl monomers included elemental and spectral analyses and identification of acetaldehyde as a product of hydrolysis. Added characterization consisted in vinyl polymerization with free radical initiators.

EXPERIMENTAL

Reaction of diethylamine, carbon disulfide, and acetylene.² Diethylamine (43.8 g.) was added to 100 ml. of tetrahydro-

furan containing carbon disulfide (45.7 g.) with cooling and shaking. Potassium hydroxide (1 g.) was added to the dithiocarbamic acid, and the mixture was transferred to a 500-ml. stainless steel rocker bomb which previously had been flushed with nitrogen. The bomb was pressure tested with nitrogen at 36 atm. pressure, then cooled in a solid carbon dioxide/methanol cooling bath and evacuated to about 10 mm. pressure. The equipment was installed behind a heavy barricade, and all operations with acetylene were controlled from the outside. With the bomb temperature slightly under room temperature, acetylene was introduced to 13 atm., and the reaction mixture was heated to 130°. This temperature was maintained for 6 hr., and the pressure was kept at 13–17 atm. by periodic repressuring with acetylene. The bomb was next cooled to room temperature, the pressure released, and the contents were removed. The reaction mixture was distilled, and the fraction distilling at 92–93°/2 mm. weighed 55 g. (52.4% yield), $n_D^{25} 1.5942$.

Anal. Calcd. for $\text{C}_7\text{H}_{14}\text{NS}_2$: C, 48.0; H, 7.4; S, 36.5; N, 8.1. Found: C, 48.1; H, 7.5; S, 36.3; N, 7.9.

The infrared spectrum showed absorption at 3.25 μ and 3.3 μ for double bond CH; 3.4 μ , 3.42 μ , and 3.5 μ for saturated CH; 6.3 μ for S—C=C<; and 6.75 μ for —N—C=S. Hydrogen deformation bands for S—CH=CH₂ compounds have not been assigned (see Fig. 1).

Vinyl *N,N*-diethyldithiocarbamate (4 g.), ethanol (17.5 ml.), and concentrated hydrochloric acid (25 ml.) were heated in an 18-inch still equipped with variable take-off. The distillate was slowly removed during 1.5 hr. and dropped into excess dinitrophenylhydrazine reagent. The dinitrophenylhydrazone, after recrystallization from ethyl acetate, weighed 2.1 g. (41%), m.p. 147–148°. The infrared spectrum was identical to that of an authentic sample of the dinitrophenylhydrazone of acetaldehyde.

Reaction of dibutylamine, carbon disulfide, and acetylene. A mixture of di-*n*-butylamine (64.5 g.) and carbon disulfide (38 g.) in tetrahydrofuran (100 ml.) containing potassium hydroxide (1 g.) was treated with acetylene under a gauge pressure of 15–17 atm. during 8.5 hr. at 135°. The reaction mixture was worked up as described previously, and 75 g. of the vinyl ester distilling at 131–138°/3 mm. (59.6% yield), $n_D^{25} 1.5543$, was obtained. On redistillation, most of this fraction distilled at 144–147°/4–5 mm., $n_D^{25} 1.5550$.

Anal. Calcd. for $\text{C}_{11}\text{H}_{21}\text{NS}_2$: C, 57.2; H, 9.1; S, 27.7. Found: C, 57.3; H, 9.3; S, 27.4.

This vinyl ester (4 g.) containing α,α' -azobis(α,γ -dimethylvaleronitrile) (0.008 g.) was heated to 95–98° for 3 hr. The resulting homopolymer was extremely viscous at room temperature. Polymerization of this vinyl monomer (4.3 g.) with α,α' -azobis(α -isobutyronitrile) initiator (0.08 g.) at 80° and 8000 atm. pressure in benzene (4.3 g.) gave a homopolymer which could be pressed into a film at 50°. At room temperature the film was clear, limp, and slightly tacky.

Quantitative hydrogenation with platinum catalyst at room temperature and atmospheric pressure in dioxane solvent gave values varying from 0.0032 to 0.0073 g. of hydrogen/g. of sample (theory—0.009 g. of hydrogen/g. of sample). It is likely that the hydrogenation was incomplete and erratic because of catalyst poisoning by this sulfur-containing compound.

Reaction of dipropylamine, carbon disulfide, and acetylene. A mixture of di-*n*-propylamine (60.7 g.), carbon disulfide (45.7 g.), and potassium hydroxide (1 g.) in tetrahydrofuran (100 ml.) was treated with acetylene under a gauge pressure of 13–18 atm. during 9 hr. at 110–150°. The reaction mixture was worked up as described previously, and 68 g. of the vinyl ester distilling at 123–124°/8 mm. (55.6% yield), $n_D^{25} 1.5721$, was obtained.

Anal. Calcd. for $\text{C}_9\text{H}_{17}\text{NS}_2$: C, 53.2; H, 8.3. Found: C, 53.2; H, 8.0.

(2) C. T. Handy and J. C. Sauer, U. S. Patent 2,579,384, December 18, 1951.

(1) M. Delephine, *Compt. rend.*, **134**, 715 (1902).