

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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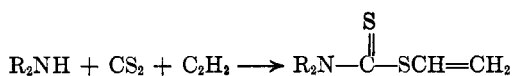
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Synthesis of Vinyl *N,N*-Dialkyldithiocarbamates

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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 $C_7H_{14}NS_2$: 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 $C_{11}H_{21}NS_2$: 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 $C_9H_{17}NS_2$: C, 53.2; H, 8.3. Found: C, 53.2; H, 8.0.

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

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

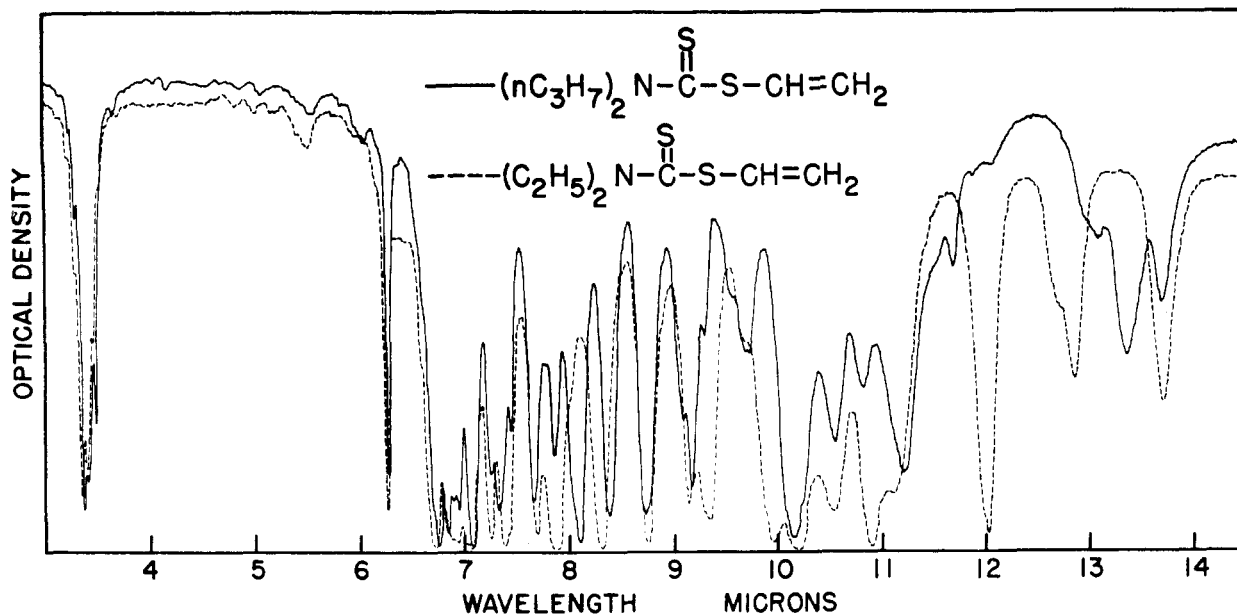


Figure 1

The infrared spectrum is very similar to that obtained for the *N,N*-diethyl analog (see Fig. 1).

Commercial-grade acetylene was purified according to a previously described procedure.³ The amines were obtained from commercial sources and purified by distillation. The infrared spectra were determined on a Perkin-Elmer 21 double-beam spectrometer.

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(3) J. C. Sauer, *J. Am. Chem. Soc.*, **79**, 5314 (1957).

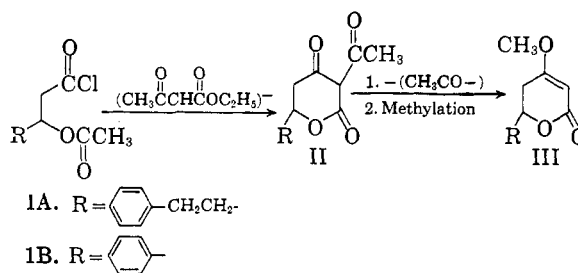
Reaction of 3-Phenyl-3-acetoxypropanoyl Chloride with Ethyl Sodioacetoacetate

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Anschütz¹ prepared 3-acetyl-4-hydroxycoumarin by treating acetylsalicyl chloride with sodioacetoacetic ester. This unique method of preparing β -ketolactones appeared promising as a method of preparing dihydrokavain, IIIA and the following reaction sequence was proposed:

(1) R. Anschütz, *Ann.*, **367**, 193 (1909).



The study of this synthetic route was undertaken using 3-phenyl-3-acetoxypropanoyl chloride, IB, as the model compound.

Two crystalline products were obtained from the reaction of ethyl sodioacetoacetate with 3-phenyl-3-acetoxypropanoyl chloride. Both products gave positive ferric chloride tests and were soluble in sodium hydroxide, but only one was soluble in sodium bicarbonate. On alkaline hydrolysis both compounds gave 3-phenyl-5-ketocaproic acid. The infrared spectrum of the sodium bicarbonate soluble material was in good agreement with the structure of 3-phenyl-4-carboethoxy-5-ketocaproic acid V; a 5.80 μ band being ascribed to the ester carbonyl groups (3-phenyl-5-ketocaproic acid has one sharp band 5.91 μ). This material had an ultraviolet absorption spectra of $\lambda_{\max}^{\text{EtOH}}$ 258 $m\mu$, ϵ 336, however in alcoholic potassium hydroxide a shift to λ_{\max} 283 $m\mu$, ϵ 12,440 was observed after one hour.

An independent synthesis of 3-phenyl-4-carboethoxy-5-ketocaproic acid, V, was undertaken and on mixed melting point with the sodium bicarbonate soluble product no depression was observed. The infrared spectrum of the sodium bicarbonate insoluble product differed greatly from V, however