Derivatives of Sulfenic Acids. XXXV. The Reaction of 2,4-Dinitrobenzenesulfenyl Chloride with Vinyl Acetate[1]

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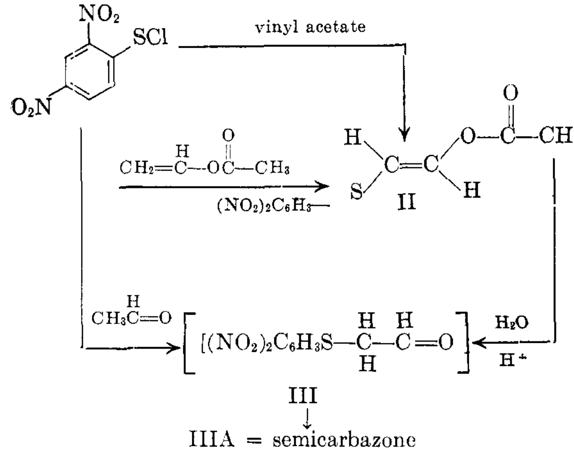
The reactions of 2,4-dinitrobenzenesulfenyl chloride (I) with olefins, acetylenes and numerous other reagents have now been studied in considerable detail,[2] but the reaction with vinyl esters has not been reported.

It has now been shown that the sulfenyl chloride (I) reacts with vinyl acetate to yield *trans*-1-acetoxy-2-(2′-4′-dinitrophenylthio)ethene, II, as the only isolatable product, in about 40% yield. The reaction was best carried out in glacial acetic acid as solvent. None of the 1:1 adduct was found, suggesting that the intermediate episulfonium ion is stabilized by electron release from the ether oxygen of the acetoxy group (compare Orr and Kharasch[3]). The relatively low yield of adduct appears to be caused by some attendant polymerization.



The proof of structure of II is based on (a) elementary analysis, (b) the infrared spectrum which showed the vinyl acetate absorption at 1755 cm.$^{-1}$ and the *trans*-hydrogen absorption at 965 cm.$^{-1}$, and (c) hydrolysis of II to the aldehyde, III, which was characterized as the semicarbazone III A (and also obtained via I and acetaldehyde).

While the reaction of I with numerous ketones gives excellently crystalline derivatives, III was generally obtained as an oil and could not be obtained as a good crystalline product. Preliminary experiments with several other aldehydes also failed to give satisfactory solid derivatives—which is an unusual circumstance for the products derived from I.[4] The hydrolysis of II to III must be conducted in acid media, since in presence of alkali, III apparently undergoes rapid polymerization. An attempt to oxidize III to the corresponding acid with alkaline permanganate was not successful, as scission of the Ar-S bond occurred under the conditions attempted to give only dinitrophenol.

It was of interest to compare the rate of reaction of I with vinyl acetate, relative to that with cyclohexene, styrene, *etc.*[5] The reaction in dry acetic acid, at 35°, followed second-order kinetics and gave a rate constant (1. × mol.$^{-1}$ × min.$^{-1}$) of 2.94 × 10^{-4}, which shows it to be only about $^1/_{300}$ as fast as styrene, for which the corresponding k is 888 × 10^{-4} (1. × mol.$^{-1}$ × min.$^{-1}$), and approximately $^1/_{3000}$ that of cyclohexene,[5] under the same conditions. A qualitative run with vinyl *n*-butyl ether also showed this reaction to proceed slowly, indicating an inductive deactivation of the olefin bond by the alkoxy group.

EXPERIMENTAL

trans-(1-Acetoxy)-2(2′,4′-dinitrophenylthio)ethene, II. —2,4-Dinitrobenzenesulfenyl chloride (23.4 g.; 0.01 mole), recrystallized from carbon tetrachloride, was dissolved in 35 ml. glacial acetic acid, and to this was added 8 ml. (0.09 mole) of vinyl acetate (Matheson Company, 99.5%, stabilized product). The mixture was let stand two days at room temperature, then evaporated to half volume, at room temperature and reduced pressure. The crude product (1.23 g., 43%) melted at 152°, and this was raised to 159°, by recrystallizing from a 1:1 mixture of 95% alcohol and ethyl acetate.

Anal. Calcd. for $C_{10}H_8O_6N_2S$: C, 42.3; H, 2.82. Found: C, 42.13; H, 3.02.

2,4-Dinitrophenylthioacetaldehyde. II (568 mg., 0.002 mole) was added to a solution made from 10 ml. water, 10 ml. 95% alcohol and 1 ml. concd. sulfuric acid. The mixture was heated at reflux until all of the insoluble material disappeared (about 1 hr.). The hot solution was filtered and cooled, whereupon formation of some oily layer was noted. The acidified aqueous solution was extracted with methylene chloride and the extract dried with anhydrous magnesium sulfate (calcium chloride as desiccant seemed to promote polymerization of III). After the solvent was evaporated, there remained a dark oily mass, which was re-extracted with ethanol. Evaporation of the alcohol left the aldehyde as a wax-like, yellow mass of crystals, 320 mg. (66%); m.p. 49°.

The aldehyde could not be obtained in analytically pure condition, as it was too subject to thermal decomposition to distill at reduced pressure, while recrystallization from other solvents gave only oily precipitates. The infrared spectrum showed the carbonyl band at 1730 cm.$^{-1}$

2,4-Dinitrophenylthioacetaldehyde semicarbazone. III (224 mg., 0.001 mole) was dissolved in 10 ml. ethanol and diluted with water until the solution became turbid. The turbidity was dispelled by adding a few drops of ethanol, then 1 g. of semicarbazide hydrochloride and 1.5 g. sodium acetate, with vigorous shaking of the reaction mixture. The reaction vessel was placed in a beaker of boiling water and left there

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[1] This study was carried out under sponsorship of the Office of Ordnance Research, United States Army, Contract DA-04-495-Ord. 901.

[2] For a summary of references *Cf.* N. Kharasch, in Organic Sulfur Compounds, Vol. I., Pergamon Press, New York-London, 1960.

[3] W. L. Orr and N. Kharasch, *J. Am. Chem. Soc.*, **78**, 1201 (1956).

[4] N. Kharasch, *J. Chem. Ed.*, **33**, 585, 1956; also R. B. Langford and D. D. Lawson, **34**, 510 (1957).

[5] D. R. Hogg and N. Kharasch, *J. Am. Chem. Soc.*, **78**, 2728 (1956).

until it cooled to room temperature. Scratching and cooling induced precipitation of the product, which was collected by filtration and recrystallized from a mixture of methanol and water. Yield: 249 mg; 83%; m.p. (dec.) 202°.

Anal. Calcd. for $C_9H_9N_5O_5S$: N, 10.71. Found: N, 10.45.

Kinetic measurements of the reaction of I with vinyl acetate, in dry acetic acid, at 35°. The determination of the second order constant, k_2, was made in the manner described by Orr and Kharasch, in dry acetic acid at 35 ± .02°, and gave a value for k_2 (l. × mol^{-1} × min^{-1}) of 2.94 × 10^{-4} ± 4%.

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Alkyl 6-Alkoxytetrahydropyran-2-carboxylates[1]

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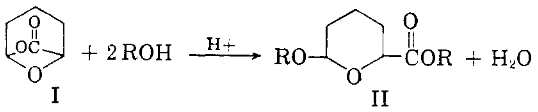
The preparation of ethyl 3,4-dihydro-2*H*-pyran-2-carboxylate[3] and the subsequent reaction with phenols to prepare ethyl 6-aryloxytetrahydropyran-2-carboxylates[4] have been reported. We wish to report the synthesis of several alkyl 6-alkoxytetrahydropyran-2-carboxylates (II) and the 2,5-dimethyl derivatives. These materials are prepared readily by the reaction of 7-oxo-6,8-dioxabicyclo [3.2.1.] octane (I) or its 1,4-dimethyl derivative with the appropriate alcohol in the presence of sulfuric acid as a catalyst and isopropyl ether as an entrainer to remove the coproduct water.

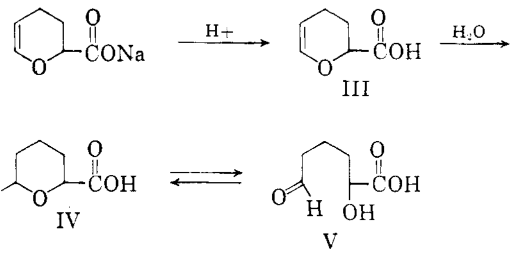


The starting lactones may be prepared from acrolein dimer or methacrolein dimer by oxidation with silver oxide[3] or oxygen,[5] by the Tishchenko reaction,[6] or by the Cannizzaro reaction.[7]

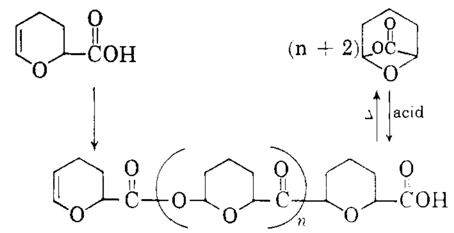
The reactant combinations that were used and the results that were obtained are shown in Table I. Good to excellent yields were obtained in all cases and the products from a single distillation were of high purity.

As a means of obtaining esters for which the alkyl groups of the ester and of the acetal functions were different, two of the acetal-esters were subjected to base-catalyzed transesterification. The reactions were conducted in a standard manner and the equilibrium was shifted by removing the exchanged alcohol by distillation. The reactant combinations used and the results obtained are summarized in Table II.

Whetstone and Ballard[3] reported that, in their attempts to isolate the free 3,4-dihydro-2*H*-pyran-2-carboxylic acid (III) by acidification of the sodium salt and extraction with ether, a viscous, water-soluble product was obtained. The acid was unstable and resinified on standing but immediate distillation provided the lactone, 7-oxo-6,8-dioxabicyclo[3.2.1]octane (I). In addition to the extracted acid, these workers isolated also a viscous solid by evaporation of the aqueous solution. On the basis of the analytical results, this material was considered to be a mixture of the hydroxy acid (IV) and 5-formyl-2-hydroxypentanoic acid (V). These materials were presumed to have formed by the acid-catalyzed hydration of the unsaturated acid (III).



We have encountered this same problem in our work even when the unsaturated acid (III) was isolated from its sodium salt under conditions designed to minimize hydration of the acid (80% acidification at 0° with mineral acid and in the presence of solvent to immediately extract the unsaturated acid.) The isolated acid resinified rapidly to form a clear, tacky solid and appeared to be in major part a homopolymer of the unsaturated acid (III), based upon analyses (elemental, functional group, and infrared) and the fact that strong heating converted the polymer to the monomeric lactone.



The lactone (I) polymerized in a few hours in the presence of ferric chloride or aluminum bromide to yield a water-insoluble polymer which appeared very similar to that obtained from the unsaturated acid (III).

The 6-hydroxytetrahydropyran-2-carboxylic acid (IV) was isolated in low yield from the aqueous solution remaining after the sodium salt had been acidi-

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(3) R. R. Whetstone and S. A. Ballard, *J. Am. Chem. Soc.*, **73**, 5280 (1951).

(4) R. R. Whetstone, U. S. Patent **2,574,444** (1951).

(5) A. E. Montagna and L. V. McQuillen, British Patent **782,430**, (1957).

(6) C. W. Smith, U. S. Patent **2,537,921** (1957).

(7) G. G. Stoner and J. S. McNulty, *J. Am. Chem. Soc.*, **72**, 1531 (1950).