The product was decomposed and worked up in the same manner as that from the rearrangement of the esters. From it there was obtained 3 g. (60%) of 2-acetyl-1-naphthol; 0.2 g. (4%) of 2,4-diacetyl-1-naphthol and about 0.2 g. (4%) of recovered 4-acetyl-1-naphthol.

On heating 10 g. of 2-acetyl-1-naphthol with 20 g. of aluminum chloride in the same manner, 9.5 g. (95%) of the starting material was recovered but no other crystalline compound could be isolated from the accompanying tar.

**2-Alkyl-1-naphthols.**—The *o*-hydroxy ketones were reduced with zinc amalgam and hydrochloric acid using the detailed procedure of Coulthard, Marshall and Pyman.[6] After refluxing from fifteen to twenty-five hours, a test portion gave no color with alcoholic ferric chloride. After cooling, the product was extracted with ether and vacuum distilled. On recrystallization from petroleum ether, fine white needles were obtained. A varying amount of a non-volatile red oil remained in the distilling flask which solidified to a brittle glass. This polymerized or oxidized material probably accounts for the low yields obtained in these reductions. It was also noted that the pure alkylnaphthols on standing in the air slowly turned to a red oil and their preservation was difficult. The physical constants of these compounds are given in Table II.

TABLE II

| 2-Alkyl-1-naphthol | Yield, % | B. p. °C. | B. p. Mm. | M. p. °C. |
|---|---|---|---|---|
| Ethyl-[a] | 60 | 128–133 | (3) | 69–70 |
| Propyl- | 50 | 133–136 | (2) | 51–52 |
| Butyl- | 63 | 145–149 | (4) | 71–72 |
| Amyl- | 50 | | | 55–56 |

| Formula | Analyses, % Calcd. C | Calcd. H | Found C | Found H |
|---|---|---|---|---|
| $C_{12}H_{12}O$ | 83.7 | 7.0 | 83.3 | 7.2 |
| $C_{13}H_{14}O$ | 83.8 | 7.6 | 83.9 | 7.8 |
| $C_{14}H_{16}O$ | 84.0 | 8.1 | 84.1 | 8.4 |
| $C_{15}H_{18}O$ | 84.1 | 8.5 | 84.3 | 8.4 |

[a] Lévy [*Compt. rend.*, **194**, 1749 (1932)] prepared this compound by the dehydrogenation of 2-ethyltetrone and gives the melting point as 68–68.5°.

## Summary

1. The fatty acid esters of $\alpha$-naphthol on heating with aluminum chloride yield 2-acyl- with a little 4-acyl-1-naphthol. The lower members of the series also give small amounts of 2,4-diacyl-1-naphthol.

2. It has been pointed out that the formation of these diacyl derivatives is not evidence against an intramolecular reaction since they might have been formed from a side reaction or by a secondary rearrangement of the initial products.

3. The preparation of some 2-alkyl-1-naphthols by the reduction of the *o*-hydroxy ketones has been described.

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(6) Coulthard, Marshall and Pyman, *J. Chem. Soc.*, 280 (1930).

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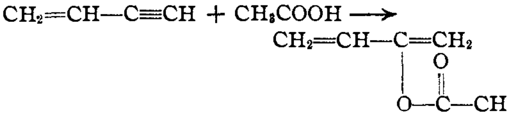
[CONTRIBUTION NO. 150 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & COMPANY]

# The Addition of Organic Carboxylic Acids to Vinylacetylene[1]

BY JAMES H. WERNTZ

Chloro-2-butadiene-1,3 (chloroprene) is obtained by the addition of hydrogen chloride to vinylacetylene.[2] The present paper is concerned with analogs of chloroprene obtained by the addition of organic acids to vinylacetylene.



$$CH_2{=}CH{-}C{\equiv}CH + CH_3COOH \longrightarrow CH_2{=}CH{-}\underset{O-\overset{\overset{O}{\|}}{C}-CH_3}{C}{=}CH_2$$

(I)

1,3-Butadienyl-2-acetate (I) is formed when vinylacetylene is added to acetic acid containing a mercuric salt or boron trifluoride. The condensation is attended by side reactions which lead to the formation of resinous substances and lower the conversion to the desired product. The ester, like chloroprene, polymerizes under normal conditions, or under high pressures, or in emulsions to form a rubber-like material. The rate of polymerization is intermediate between that of chloroprene and isoprene. Unlike chloroprene, the ester polymerizes under the influence of peroxide catalysts to form resinous polymers. The ester and its rubber-like polymer have a tendency to decompose slowly and to liberate free acid, particularly at increased temperatures.

The addition of organic carboxylic acids to vinylacetylene appears to be a general reaction. Esters obtained in this manner are listed in Table I.

**Proof of Structure of 1,3-Butadienyl-2-acetate.**—The boiling range, 38–40°, at 20 mm. of 1,3-butadienyl-2-acetate indicates it to be a mono ester since the diacetates of butenediol that are described in the literature all boil above 100° at

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(1) Paper XXII in the series "Acetylene Polymers and their Derivatives." Paper XXI, THIS JOURNAL, **56**, 1625 (1934).

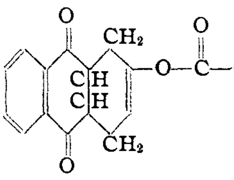
(2) Carothers, Berchet and Collins, *ibid.*, **54**, 4066 (1932)

TABLE I

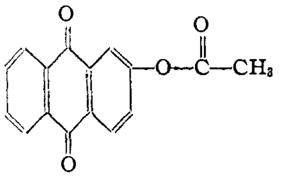
PHYSICAL CONSTANTS AND ANALYTICAL DATA FOR SOME ESTERS OF 1,3-BUTADIENOL-2

| | | Ester | | | |
|---|---|---|---|---|---|
| | | Formate | Acetate | Chloro-acetate | Butyrate |
| B. p. | °C. | 48-49 | 52-54 | 51-53 | 59-60 |
| | mm. | 51 | 40 | 2 | 11 |
| $d_4^{20}$ | | 0.9744 | 0.9643 | 1.1676 | 0.9369 |
| $n_D^{20}$ | | 1.4539 | 1.4433 | 1.4783 | 1.4418 |
| $M_R$ | Calcd. | 26.2 | 30.8 | 35.7 | 39.9 |
| | Found | 27.3 | 30.8 | 35.4 | 39.5 |
| Carbon | Calcd. | 61.2 | 64.3 | | 68.6 |
| | Found | 62.9 | 62.8 | | 66.6 |
| Hydrogen | Calcd. | 6.1 | 7.1 | | 8.6 |
| | Found | 6.7 | 7.2 | | 8.9 |
| Chlorine | Calcd. | | | 24.2 | |
| | Found | | | 24.9 | |
| Mol. wt. in benzene | Calcd. | 98 | 112 | | 140 |
| | Found | 95 | 109 | | 138 |

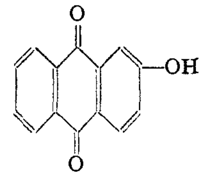
20 mm.[3] The empirical analysis confirms this observation and the determined molecular weight establishes the ester to be the monomeric form. The structure of the ester was demonstrated by its reaction with 1,4-naphthoquinone to form the crystalline addition product (II) which was oxidized to the corresponding acetoxyanthraquinone (III) and hydrolyzed finally to beta-hydroxyanthraquinone (IV). Further evidence of the assigned formula (I) was obtained by acid hydrolysis of the ester to 1,3-butadienol-2, which immediately tautomerized to methyl vinyl ketone, characterized by conversion to methyl-3-phenyl-1-pyrazoline (V).



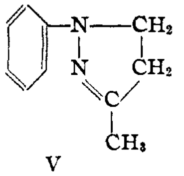
II



III



IV



V

## Experimental Part

**1,3-Butadienyl-2-acetate.**—The apparatus consisted of a one-liter 3-necked flask provided with a high-speed stirrer (2000-3000 r. p. m.), a thermometer, a jacketed, calibrated dropping funnel which was cooled with a solid carbon dioxide-acetone mixture and a reflux condenser through which ice water was circulated.

Twenty grams of mercuric oxide was dissolved in 400 g. of hot glacial acetic acid and the solution was placed in the apparatus and cooled to 20°. A cold mixture of 18 g. of fuming sulfuric acid and 30 g. of acetic anhydride was added slowly to the rapidly agitated mercuric acetate solution. The reaction mixture was then cooled to 14° and 310 g. of vinylacetylene was added as liquid from the calibrated dropping funnel to the rapidly agitated reaction mixture during the course of four hours. The reaction temperature was dropped to 5° in about half an hour, where it was held during the reaction by means of an ice bath. The reaction mixture was poured into water saturated with salt, the water-insoluble layer was neutralized with ammonium hydroxide and finally was washed with saturated salt solution. After drying over calcium chloride the product was fractionated under reduced pressure and 80 g. of crude 1,3-butadienyl-2-acetate boiling 30-80° at 20 mm. was obtained which amounted to a conversion of 11.9% based on the vinylacetylene used. Refractionation of the crude 1,3-butadienyl-2-acetate yielded 36 g. distilling at 38-40° at 20 mm. Sixty-four grams of resin was isolated from the reaction mixture and a considerable amount of polymer formed during the distillation of the ester in the presence of hydroquinone.

In experiments carried out at 50°, 9% of 1,3-butadienyl-2-acetate, 9% of a higher boiling unsaturated liquid and 12% of resin were obtained but the formation of the last two products was suppressed by the use of a high boiling gasoline as a diluent. Better results were obtained with the mercuric sulfate-sulfoacetic acid catalyst than with mercuric sulfate or boron trifluoride. The use of the latter catalyst led to the formation of 6% of 1,3-butadienyl-2-acetate, 14% of a higher boiling unsaturated liquid and 15% of resin.

**Esters of Formic, Butyric and Chloroacetic Acids.**—The formic and chloroacetic esters were prepared using mercuric phosphate as the catalyst; the butyric ester was prepared by means of the mercuric sulfoacetate catalyst. Large quantities of resins were formed during the reactions and subsequent distillations and conversions were in all cases poorer than obtained for the acetic ester. The liberation of free acid was also noted during the distillation of these esters over hydroquinone.

**Methyl-3-phenyl-1-pyrazoline** (V).—1,3-Butadienyl-2-acetate (5 g.) was heated on a water-bath with 5% sulfuric acid (50 g.) and yielded, in addition to a soft, water-insoluble resin, methyl vinyl ketone which was isolated by distillation with steam. When mixed with phenylhydrazine an oil formed which slowly solidified and was recrystallized from alcohol. The needle-like crystals (2.5 g.) melted 75-76° which is in good agreement with the value previously reported for methyl-3-phenyl-1-pyrazoline.[4]

*Anal.* Calcd. for $C_{10}H_{12}N_2$: C, 75; H, 7.5. Found: C, 73.7; H, 7.6.

**Beta-Hydroxyanthraquinone** (IV).—1,3-Butadienyl-2-acetate (1 g.) stabilized with hydroquinone was heated at

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[3] Diacetate of 3,4-dihydroxybutene-1, b. p. 110° at 20 mm., Henninger, *Ann. chim. phys.*, [6] **7**, 214 (1886); diacetate of 1,1-dihydroxybutene-2, b. p. 150-160° at 20 mm., *Russischen Chem. Gesellschaft*, **11**, 79 (1872); diacetate of 2,3-dihydroxybutene-2, b. p. 110-115° at 29 mm., Bouveault and Locquin, *Bull. soc. chim.*, [3] **35**, 635 (1906).

[4] Ach, *Ann.*, **253**, 56 (1889), and Maire, *Bull. soc. chim.*, [4] **3**, 272 (1908).

100° for one and one-half hours with 1,4-naphthoquinone (0.5 g.). The tetrahydro compound (II) which crystallized on cooling was dissolved in dilute alcoholic sodium hydroxide, and a rapid stream of air was bubbled into the solution for one and one-half hours. Yellow colored crystals precipitated which melted at about 170°. When recrystallized from hot alcohol a fine yellow powder was obtained which melted at about 165° but further recrystallization of the crude acetoxyanthraquinone (III) did not yield a sharply melting product.[5]

The crude acetoxyanthraquinone was converted to hydroxyanthraquinone (IV) by heating at 100° for two hours with dilute alcoholic potassium hydroxide. On concentrating the alcohol solution a dark brown powder separated which was recrystallized from alcohol containing some water. The yellow needles melted at 297° (uncorr.).[6] A mixture of this compound with beta-hydroxyanthraquinone (m. p. 298°) obtained by hydrolysis of beta-ethoxyanthraquinone melted at 296° (uncorr.). Beta-hydroxyanthraquinone (m. p. 299°) was also synthesized by condensation of phthalaldehydic acid with phenol, followed by reduction, ring closure and oxidation.[7] A mixture of this sample with the hydroxyanthraquinone derived from 1,3-butadienyl-2 acetate melted at 297–299° (uncorr.).

**Polymerization of Esters of 1,3-Butadienol-2.**—1,3-Butadienyl-2-acetate polymerizes in about ten days at room temperature in the presence of air to form a rubber-like material. Sometimes under certain undetermined conditions granular polymers are also formed. Polymerization is retarded by blanketing with carbon dioxide or nitrogen or by introducing small amounts of pyrogallol or hydroquinone. In a solution containing equal parts of the ester and toluene, 7.5% polymerization is obtained in four days at room temperature, 17.9% in seven days and 32% in twelve days as compared with 7.6% polymerization in one hour at 100° and 37% polymerization in one hour at 145°. The calculated unimolecular reaction velocity constant is 0.001112 (in hours at room temperature for a 50% solution in toluene) which is about 230 times greater than that calculated for isoprene but only about one-third the value calculated for chloro-2-butadiene-1,3.[8] Benzoyl peroxide catalyzes polymerization at room temperature; at 100° the catalytic effect is even more marked (72% polymerization to a resin-like polymer of the ester in an equal part of toluene in one hour). When uranyl nitrate is present during exposure to sunlight, 89% polymerization of the acetate is obtained in one week. Pressure has a marked effect on the rate of polymerization; 1,3-butadienyl-2-acetate containing pyrogallol as an antioxidant yields 72% of rubber-like polymer when subjected to a pressure of 5000 atmospheres for seventeen and one-half hours at 57°.[9] Aqueous emulsions of the ester made with sodium oleate give films of rubber-like material on evaporation of the water. The soluble polymers which result when the esters of 1,3-butadienol-2 are polymerized in solution form clear, homogeneous films when the solvent evaporates. The formic, chloroacetic and butyric esters polymerize at room temperature at least as rapidly as the acetic ester.

**Acknowledgment.**—The author wishes to acknowledge the assistance of Mr. George F. Hennion of the University of Notre Dame and of Dr. H. B. Dykstra and Dr. P. R. Austin of this Laboratory in the characterization of 1,3-butadienyl-2-acetate.

## Summary

The formic, acetic, chloroacetic and butyric esters of 1,3-butadienol-2 were prepared from vinylacetylene and the corresponding acid. These esters polymerized to form rubber-like and resin-like polymers. The structure of 1,3-butadienyl-2-acetate was established through (a) hydrolysis to methyl vinyl ketone and (b) through its reaction with alpha-naphthoquinone to form a crystalline addition product which was oxidized and hydrolyzed to beta-hydroxyanthraquinone.

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[5] Liebermann, *Ann.*, **212**, 52 (1882), gives the m. p. of III as 159° and, in *Ber.*, **15**, 1804 (1882), reports the acetate of alpha-hydroxy-9,10-anthraquinone to melt at 176–179°.

[6] Liebermann, *Ann.*, **212**, 25 (1882), reports 302° as the m. p. of IV.

[7] Brubaker and Adams, THIS JOURNAL, **49**, 2279 (1927).

[8] Carothers, *Ind. Eng. Chem.*, **26**, 30 (1934).

[9] Unpublished experiment made by Dr. H. W. Starkweather of this Laboratory.