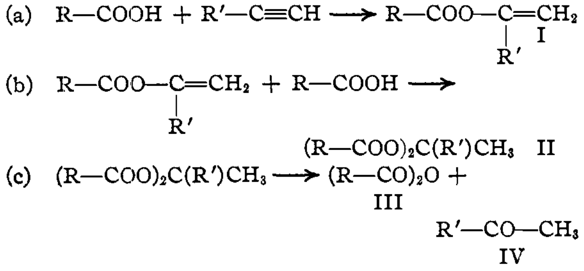
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

The Addition of Some Organic Acids to Alkyl Acetylenes

BY G. F. HENNION AND J. A. NIEUWLAND

Introduction

In several recent communications[1,2,3] from our laboratories it has been reported that alkyl acetylenes react with organic oxy compounds, in the presence of small amounts of boron fluoride and mercuric oxide, to form addition compounds. Methyl alcohol and glycol thus yield ketone acetals and the simple organic acids form alkenyl esters. The reaction leading to alkenyl esters has now been studied in greater detail and esters have been prepared from methyl, butyl and amyl acetylenes. A varying amount of ketone[1] was usually obtained as a by product. The following reactions probably occur more or less simultaneously



$$\text{(a)}\quad R\text{—}COOH + R'\text{—}C{\equiv}CH \longrightarrow \underset{\text{I}}{R\text{—}COO\text{—}\underset{\displaystyle R'}{\underset{|}{C}}{=}CH_2}$$

$$\text{(b)}\quad R\text{—}COO\text{—}\underset{\displaystyle R'}{\underset{|}{C}}{=}CH_2 + R\text{—}COOH \longrightarrow (R\text{—}COO)_2C(R')CH_3 \quad \text{II}$$

$$\text{(c)}\quad (R\text{—}COO)_2C(R')CH_3 \longrightarrow \underset{\text{III}}{(R\text{—}CO)_2O} + \underset{\text{IV}}{R'\text{—}CO\text{—}CH_3}$$

Very recently a patent[4] has been obtained by the I. G. Farbenindustrie covering the preparation of anhydrides and ketones (III and IV) from certain alkylacetylenes. The reactions were apparently not carried out so as to form primarily esters of types I or II, and, in fact, such esters are not mentioned. We have been able to prepare the esters of type I in 30–68% yield but have been unable to isolate those of type II. It may be that they spontaneously break down in accordance with reaction (c).

The esters isolated, along with their physical properties, yields and analyses, are reported in Tables I, II and III. In these tables R represents the alkyl group originating in the acid and R′ the group attached to the ethynyl group of the acetylene used. Vinyl acetate and its constants[5] have been included for the sake of comparison.

TABLE I

ALKENYL ESTERS, $R\text{—}COO\text{—}C(R'){=}CH_2$

No.	R	R′	Compound	Yield, %
1	CH_3–	H	Vinyl acetate	. .
2	CH_3–	CH_3–	2-Acetoxypropene-1	30
3	CH_3–	n-C_4H_9–	2-Acetoxyhexene-1	31
4	CH_3–	n-C_5H_{11}–	2-Acetoxyheptene-1	34
5	CH_2Cl–	n-C_4H_9–	2-(Chloroacetoxy)-hexene-1	68
6	C_6H_5–	n-C_4H_9–	2-(Benzoyloxy)-hexene-1	44

TABLE II

PROPERTIES OF ALKENYL ESTERS

No.	B. p., °C.	Mm.	Density	n_D	MR'_D Calcd.	MR'_D Found
1	73		0.9342_{20}	1.3958_{20}	21.86	22.15
2	92–94	736	$.9090_{20}$	1.4033_{20}	26.47	26.73
3	74–75	39	$.8874_{26}$	1.4176_{26}	40.34	40.31
4	92–94	40	$.8800_{25}$	1.4217_{25}	44.95	45.06
5	100–101	20	1.017_{26}	1.4453_{26}	45.3	46.2
6	147–149	21	0.984_{27}	1.4998_{27}	59.82	61.0

TABLE III

ANALYSES OF ALKENYL ESTERS

No.	Empirical formula	Calcd., % C	Calcd., % H	Found, % C	Found, % H
2	$C_5H_8O_2$	59.96	8.05	58.5	8.05
3	$C_8H_{14}O_2$	67.55	9.93	67.42	9.6
4	$C_8H_{13}ClO_2$	Cl	20.01	Cl	19.9
6	$C_{13}H_{16}O_2$	76.44	7.90	75.9	7.7

Experimental

Reagents.—The boron fluoride required as a catalyst was used as the ether compound, $(C_2H_5)_2O \cdot BF_3$. The preparation of this compound, b. p. 125–126°, has been described.[6] Methylacetylene was prepared by the action of dimethyl sulfate on sodium acetylide in liquid ammonia. It was obtained free from ammonia and water by passing the gas through water, dilute sulfuric acid, a calcium chloride tower and finally through soda lime. Methylacetylene was used in the gaseous state by passing directly into mechanically stirred acetic acid containing the usual catalyst. Absorption was quite rapid and cooling with an ice-bath was occasionally necessary.

Butyl- and amylacetylenes, b. p. 70–71° and 97–99°, respectively, were prepared by a modification of the Picon synthesis,[7] using sodium acetylide and the appropriate alkyl bromide.

Acetic acid, chloroacetic acid and benzoic acid were C. P. products. They were better than 99.6% pure on the basis of titration with standard alkali.

Action of Butylacetylene on Chloroacetic Acid.—Into a 500-ml. three-necked flask was weighed 3 g. of red mercuric oxide. To this was added 2 ml. of the ether–boron fluoride compound and 2 ml. of absolute methyl alcohol.

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[1] Hennion, Killian, *et al.*, THIS JOURNAL, **56**, 1130 (1934).

[2] Killian, Hennion and Nieuwland, *ibid.*, **56**, 1384 (1934).

[3] Killian, Hennion and Nieuwland, *ibid.*, **56**, 1786 (1934).

[4] German Patent 590,237; issued Jan. 4, 1934. (This patent was brought to the attention of the authors after the present work had been completed.)

[5] Morrison and Shaw, *Chem. and Met. Eng.*, **40**, 296 (1933).

[6] Hennion, Hinton and Nieuwland, THIS JOURNAL, **55**, 2858 (1933).

[7] Picon, *Compt. rend.*, **158**, 1346 (1914); **169**, 32 (1919).

The mixture was warmed slightly to partially dissolve the mercuric oxide. The flask was equipped with a mercury-sealed stirrer, a dropping funnel, and a reflux condenser. One-half mole (47.3 g.) of chloroacetic acid was added to the catalyst, the stirrer started, and 55 g. (excess) of butylacetylene added dropwise through the dropping funnel. The chloroacetic acid soon liquefied and an ice-bath was placed around the flask. The addition of butylacetylene required about one-half hour. Stirring was continued for another half hour at room temperature. After stirring, the flask was removed, 60 ml. of ether added and the mixture washed three times with 50-ml. portions of ice water and then with 50-ml. portions of cold 10% sodium carbonate solution until all unreacted acid had been removed. The ether extract was dried over calcium chloride, the ether removed by distillation, and the residue fractionated *in vacuo* at 20 mm. through a 30-cm. Vigreux style column. The yield of 2-(chloroacetoxy)-hexene-1 amounted to 60 g.

Action of Butylacetylene on Benzoic Acid.—The catalyst was prepared as described above, 61 g. (0.5 mole) of solid benzoic acid added, the stirrer started, and 82 g. (double the theoretical quantity) of butylacetylene added dropwise. The benzoic acid did not liquefy readily; consequently, after about one-fourth of the acetylene had been added, the flask was heated over a burner. The reaction then proceeded very vigorously. The remaining acetylene was added in a rapid stream of drops, heating at reflux temperature being maintained for one hour. Upon cooling the flask contents remained completely liquid. The ester was isolated as described above; yield, 45 g.

Proof of Structure of Alkenyl Esters.—The fact that the acyloxy attachments occur at the second carbon atom of the alkylacetylenes was shown by saponification[1] with alcoholic potash. The ketones formed, with the exception of acetone, were identified by their physical properties and by the melting points of their semicarbazones. Acetone, obtained from 2-acetoxypropene-1, was identified by the iodoform reaction and by the nitroprusside test.

Properties of Alkenyl Esters.—With the exception of 2-acetoxypropene-1, the esters described possess a characteristic, not unpleasant, odor. Acetoxypropene has a rather sharp odor. All of these esters were found to be quite stable. Some of these have been kept for over a year without any indication of polymerization. Apparently the alkyl group in the α position of the vinyl group exerts a marked stabilizing effect.

Summary

1. Monobasic organic acids react with monoalkyl acetylenes by direct addition, the main reaction being mole for mole addition. The acyloxy group attaches itself to the second (non-terminal) acetylenic carbon atom.

2. Five such addition compounds (alkenyl esters) are described, these being prepared from acetic, chloroacetic and benzoic acids with methyl-, butyl- and amylacetylenes.

NOTRE DAME, INDIANA

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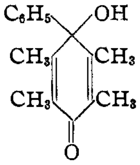
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, VASSAR COLLEGE]

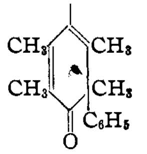
Isomeric Forms of 2,3,5,6-Tetramethyl-3-phenylcyclohexene-5-dione-1,4

BY H. MARJORIE CRAWFORD

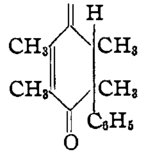
In an earlier paper[1] on the reaction between duroquinone and phenylmagnesium bromide, three compounds ($C_{16}H_{18}O_2$) resulting from the addition of one mole of phenylmagnesium bromide to one mole of duroquinone were described. They were assigned the following structures



203°



150°

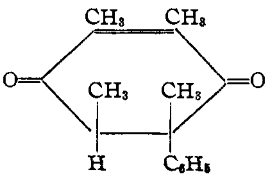


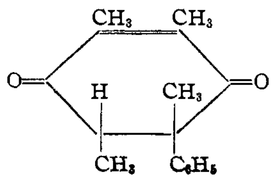
142°

Mention was also made of a pale yellow compound, melting at 62°, which was obtained when attempts were made to form the semicarbazone of the 142° compound. This low-melting substance was obtained in very small amounts, and aside from carbon and hydrogen analyses, very little was known about it.

In the present investigation, working with larger amounts of material, it is shown that the melting point is somewhat higher (72° instead of 62°), and that this low-melting compound and the one melting at 142° have the same molecular formula.

When this 72° compound was first encountered, we suggested that it is a geometric isomer of the 142° substance (2,3,5,6-tetramethyl-3-phenylcyclohexene-5-dione-1,4), which is the only one of the three monoaddition products capable of existing in two geometric forms





(1) Smith and Crawford, THIS JOURNAL, 50, 869 (1928).