mine the rate of interchange of the oxalate in chromioxalate ions with added oxalate ions. If, however, the racemization does not involve an ionization then the rates of the inversion and interchange can be widely different. At a temperature of 35° the half-time for the inversion of *d*-chromioxalate ion has been calculated to be about twenty-four minutes. If the inversion of configuration of chromioxalate ion is paralleled by an interchange with oxalate ion in solution, then in a solution containing 0.06 molar chromioxalate ions and 0.012 molar radioactive oxalate ions, the radioactive oxalate should show a loss in radioactivity due to interchange alone of well over 50% in twelve minutes and of over 80% in twenty-five minutes. The results given in Tables I and II show that there is probably no loss in radioactivity after twenty-five minutes or, at most, only a very slight loss. This seems to indicate rather clearly that the mechanism of the racemization does not involve an ionization step.

To explain the racemization the only alternative at present seems to be some sort of intramolecular rearrangement. A plausible scheme is the one proposed by Werner[9] in his original re-

(9) Werner, *Ber.*, **45**, 3061 (1912).

port on optically active potassium chromioxalate. Werner suggested that the racemization might involve the breaking of only one of the bonds of one of the oxalate ions. The resulting pyramidal structure could then undergo an inversion of configuration and eventually give a racemic product. This is, however, only one of several possible mechanisms, and the available information does not seem to allow a choice to be made. It is hoped that a kinetic investigation of the racemization reaction will throw more light on this interesting question.

Conclusion

The interchange of oxalate ions with chromioxalate ions in aqueous solution has been investigated with the use of radio-carbon. At a temperature of 35° the exchange of oxalate ions is negligibly small. This result indicates that the racemization of the optically active chromioxalate ion, which under the same conditions is quite rapid, does not take place by a mechanism which involves an ionization of the coördination complex.

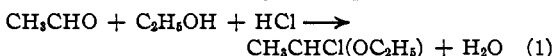# The Preparation of α-Alkyl-β-alkenylacetylenes[1]

BY W. F. ANZILOTTI AND R. R. VOGT

Introduction

α-Alkyl-β-vinylacetylenes have been prepared by Carothers and Jacobson[2] through the interaction of the sodium salt of monovinylacetylene and alkyl bromides in liquid ammonia. Truchet[3] prepared α-allyl-β-amylacetylene by the reaction of allyl benzenesulfonate with the sodium salt of 1-heptyne. Merling[4] obtained compounds of the type $CH_2=C(R)C\equiv CH$ in the desaturation of acetylenic carbinols prepared by the condensation of sodium acetylide and ketones. The preparation of compounds of the type $RCH=CH—C\equiv CH$ was not satisfactory due to poor yields of the acetylenic carbinols resulting from

(1) Paper XXX on the chemistry of the alkylacetylenes and their derivatives; previous paper, THIS JOURNAL, **60**, 2882 (1938).
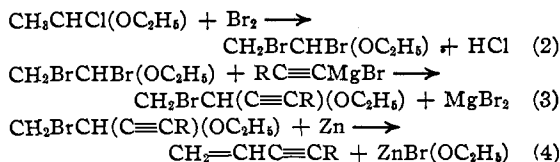
(2) Jacobson and Carothers, *ibid.*, **55**, 1622 (1933).

(3) Truchet, *Compt. rend.*, **191**, 854 (1930).

(4) Merling, Farbenfabriken vorm. F. Bayer and Co., German Patent 290,558; *Friedl.*, **12**, 61.

the condensation of sodium acetylide and aldehydes. Lespieau and Guillemonat[5] obtained divinylacetylene by the action of zinc dust on 1,6-dibromo-2,5-diethoxy-3-hexyne.

Dykstra, Lewis and Boord[6] have shown that α,β-dibromoethyl ethers react with alkylmagnesium bromides to give the corresponding β-bromo ethers, which, upon desaturation with zinc dust, give fair yields of olefins. The present paper is concerned with the reactions of alkynylmagnesium bromides and α,β-dibromoethyl ethers and subsequent desaturation of the resulting β-bromoalkynyl ethers, to give the corresponding α-alkyl-β-alkenylacetylenes. The syntheses can be shown by the equations

$$CH_3CHO + C_2H_5OH + HCl \longrightarrow$$
$$CH_3CHCl(OC_2H_5) + H_2O \quad (1)$$

(5) Lespieau and Guillemonat, *Compt. rend.*, **195**, 245 (1932).

(6) Dykstra, Lewis and Boord, THIS JOURNAL, **52**, 3396 (1930).

$$CH_3CHCl(OC_2H_5) + Br_2 \longrightarrow$$
$$CH_2BrCHBr(OC_2H_5) + HCl \quad (2)$$
$$CH_2BrCHBr(OC_2H_5) + RC \equiv CMgBr \longrightarrow$$
$$CH_2BrCH(C \equiv CR)(OC_2H_5) + MgBr_2 \quad (3)$$
$$CH_2BrCH(C \equiv CR)(OC_2H_5) + Zn \longrightarrow$$
$$CH_2 = CHC \equiv CR + ZnBr(OC_2H_5) \quad (4)$$

Reactions (1) and (2) have been discussed in detail by Dykstra, Lewis and Boord.[6] Reaction (3) is controlled by employing an excess of ether as a solvent. The yields are fair; however, the β-bromoalkynyl ethers decompose upon distillation and it was found advisable to desaturate without purification. Reaction (4) proceeds rather smoothly with refluxing, giving high yields of α-alkyl-β-alkenylacetylenes, which distil as colorless liquids having characteristic odors. In all cases of desaturation small amounts of polymer were noticeable. However, a product boiling over one degree was obtainable upon redistillation.

The method of Merling[4] is somewhat specific for compounds of the type RCH=C(R')C≡CH, while compounds of the CH_2=CHC≡CR type can be prepared by the method of Jacobson and Carothers.[2] The method herein described may be utilized, by employing the proper α,β-dibromoethyl ether, as a general procedure for the preparation of conjugate eneynes of the general formula RCH=CH—C≡CR'. The experimental data are shown in Tables I and II.

TABLE I

PHYSICAL PROPERTIES OF RCH=CH—C≡CR'

No.	R	R'	Yield, %	B. p., °C.	Mm.	d^{25}	n_D^{25}
1	H	n-C₃H₇	77	44.3–44.7	75	0.7671	1.4520
2	H	n-C₄H₉	73	61.5–62.0	60	.7579	1.4505
3	H	n-C₅H₁₁	76	27.7–28.2	4	.7602	1.4487
4	H	n-C₆H₁₃	74	45.0–45.4	4	.7872	1.4565
5	H	n-C₈H₁₇	73	77.5–78.0	4	.7858	1.4510
6	CH₃	n-C₄H₉	70	70.0–70.5	29	.7832	1.4590
7	CH₃	n-C₅H₁₁	73	54.5–55.0	5	.7850	1.4609

TABLE II

ANALYSES OF α-ALKYL-β-ALKENYLACETYLENES

No.	Empirical formula	Calcd., % C	Calcd., % H	Found, % C	Found, % H	MR Calcd.	MR Obsd.	Exal.
1	C₇H₁₀	89.3	10.7	88.9	10.6	32.06	33.08	1.02
2	C₈H₁₂	88.8	11.2	87.8	11.8	36.68	38.33	1.65
3	C₉H₁₄	88.4	11.5	87.6	12.1	41.30	43.03	1.73
4	C₁₀H₁₆	88.2	11.8	87.3	11.8	45.92	47.02	1.10
5	C₁₂H₂₀	87.7	12.3	87.3	12.5	55.15	56.25	1.10
6	C₉H₁₄	88.4	11.5	88.0	11.6	41.29	42.62	1.33
7	C₁₀H₁₆	88.2	11.8	87.9	12.1	45.92	47.00	1.08

Experimental Part

Haloethers.—α,β-Dibromoethyl ethyl ether and α,β-dibromopropyl ethyl ether were prepared according to the method of Swallen and Boord.[7]

(7) Swallen and Boord, *ibid.*, **52**, 654 (1930).

n-Alkyl-ethynylmagnesium Bromide.—A 2-liter, three-necked flask was fitted with a water-cooled condenser, sealed stirrer and a dropping funnel. Magnesium turnings (14.6 g., 0.6 mole) together with 300 ml. of anhydrous ether was added to the flask. The calculated amount of ethyl bromide was then added dropwise and the mixture finally refluxed on a water-bath for one hour. Six-tenths (0.6) mole of n-alkylacetylene was then added dropwise and, after addition, the reaction mixture refluxed on a water-bath for two hours and allowed to stand overnight. n-Propyl, n-butyl, n-amyl, n-hexyl, and n-octyl ethynylmagnesium bromides were so prepared.

1-Bromo-2-ethoxy-3-alkynes.—One hundred sixteen grams (0.5 mole) of α,β-dibromoethyl ethyl ether was diluted with four times its volume of anhydrous ether and the resulting solution slowly added to the reaction mixture from above. After the addition the reaction mixture was refluxed on a water-bath for three hours. Constant agitation was maintained throughout the course of the reaction. The reaction mixture was decomposed by pouring on ice and acidifying with dilute hydrochloric acid. The ether layer was separated, dried over calcium chloride and the ether removed by distillation. The yields of crude product based on α,β-dibromoethyl ethyl ether were, respectively; 1-bromo-2-ethoxy-3-heptyne, 80%; 1-bromo-2-ethoxy-3-octyne, 86%; 1-bromo-2-ethoxy-3-nonyne, 84%; 1-bromo-2-ethoxy-3-decyne, 88%; 1-bromo-2-ethoxy-3-dodecyne, 85%. 2-Bromo-3-ethoxy-4-nonyne, 81%, and 2-bromo-3-ethoxy-4-decyne, 84%, were prepared by employing α,-β-dibromopropyl ethyl ether.

α-Alkyl-β-alkenylacetylenes.—The crude product from above was transferred to a 2-liter, three-necked flask fitted with a reflux condenser and sealed stirrer, and three times its volume of 90% ethyl alcohol added. Three equivalents of zinc dust were added portion-wise, and the whole refluxed at the boiling point for ninety-six hours, constant agitation being maintained at all times. After the refluxing period the zinc was removed by filtration and the alcohol filtrate diluted with 8 to 10 volumes of cold dilute hydrochloric acid solution. The upper oily layer was separated, dried over calcium chloride and distilled under reduced pressure.

Summary

A method is described for the synthesis of α-alkyl-β-alkenylacetylenes in good yields. The intermediate 1-bromo-2-ethoxy-3-alkynes decompose on distillation. Purification is not necessary and desaturation may be carried out with the crude product. The compounds prepared were: 1-propyl-2-vinylacetylene, 1-butyl-2-vinylacetylene, 1-amyl-2-vinylacetylene, 1-hexyl-2-vinylacetylene, 1-octyl-2-vinylacetylene, 2-nonen-4-yne, 2-decen-4-yne. The method may be utilized in the synthesis of compounds of the general formula RCH=CHC≡CR'.