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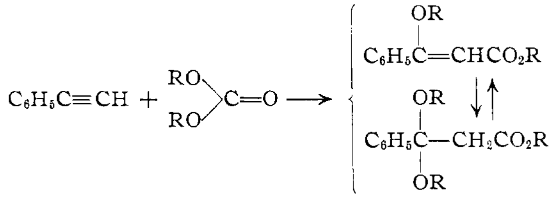
Condensation of Acetylenes with Esters. Mono Substituted Acetylenes and Alkyl Carbonates[1]

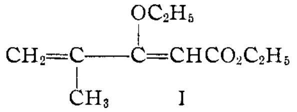
BY W. J. CROXALL AND MARIAN F. FEGLEY

The nature of the products obtained from acetylene and alkyl carbonates[1] suggested that similar results might be obtained with substituted acetylenes. Our first experiments involved sodium phenylacetylide and ethyl carbonate and it was found that when these reactants were used in equimolecular amounts intractable oils were obtained as reported earlier by Nightingale and Wadsworth.[2] However when ethyl carbonate in the presence of a basic condensation agent such as sodium phenylacetylide was treated with phenylacetylene, there was formed in good yield ethyl β-phenyl-β-ethoxyacrylate and ethyl β-phenyl-β,β-diethoxypropionate. The yield data indicated that sodium phenylacetylide functioned as a catalyst. Sodium ethoxide and benzyltrimethylammonium ethoxide were also used successfully as the basic condensation agents for this reaction in place of sodium phenylacetylide. Extension of this work to methyl carbonate gave the corresponding methyl analogs. The over-all reaction may be represented as



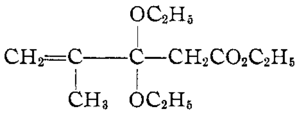
$$C_6H_5C{\equiv}CH + (RO)_2C{=}O \longrightarrow \left\{ \begin{array}{l} C_6H_5C(OR){=}CHCO_2R \\ \quad \downarrow\uparrow \\ C_6H_5C(OR)_2{-}CH_2CO_2R \end{array} \right.$$

Similar results were obtained with an alkeneyne. Ethyl carbonate and 2-methyl-1-butene-3-yne in the presence of either sodium ethoxide or benzyltrimethylammonium ethoxide gave three fractions on distillation. The first fraction was shown to be a mixture consisting chiefly of 2-methyl-3-ethoxy-4-carbethoxy-1,3-butadiene (I) containing a small amount of 2-methyl-3,3-diethoxy-4-carbethoxy-1-butene (II). This mixture when heated with a catalytic amount of sodium bisulfate gave ethanol and the pure butadiene ester (I) which was hydrogenated to the known 2-methyl-3-ethoxy-4-carbethoxybutane (III).[3] The second fraction was the butene ester (II) which on acid hydrolysis produced methyl isopropenyl ketone. Distillation of the ester (II) from a trace of sodium bisulfate gave the butadiene ester (I) and ethanol. Butene ester (II) gave on hydrogenation 2-methyl-3,3-diethoxy-4-carbethoxybutane (IV) which on acid hydrolysis yielded methyl isopropyl ketone. The third fraction was a high boiling oil which could not be distilled without decomposition. It was not characterized.



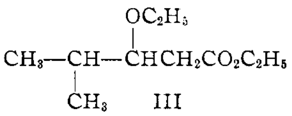
$$CH_2{=}C(CH_3){-}C(OC_2H_5){=}CHCO_2C_2H_5$$

I



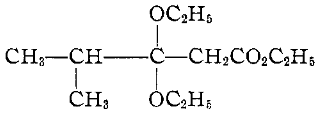
$$CH_2{=}C(CH_3){-}C(OC_2H_5)_2{-}CH_2CO_2C_2H_5$$

II



$$CH_3{-}CH(CH_3){-}CH(OC_2H_5)CH_2CO_2C_2H_5$$

III



$$CH_3{-}CH(CH_3){-}C(OC_2H_5)_2{-}CH_2CO_2C_2H_5$$

IV

These reactions are thought to proceed through a mechanism similar to that advanced for acetylene and alkyl carbonates[1] and may be represented in a condensed form as

$$RC{\equiv}CH + \overset{\ominus}{O}R \rightleftarrows RC{\equiv}\overset{\ominus}{C} + HOR$$

$$RC{\equiv}\overset{\ominus}{C} + (RO)_2CO \rightleftarrows RC{\equiv}CCO_2R + \overset{\ominus}{O}R$$

$$RC{\equiv}CCO_2R + HOR \longrightarrow$$

$$\underset{OR}{RC}{=}CHCO_2R \underset{+HOR}{\rightleftarrows} RC(OR)_2CH_2CO_2R$$

It is to be noted that this mechanism requires that the acetylene possess at least one acetylenic hydrogen atom. Actually, experiment showed that methylphenylacetylene gave no reaction.

Acknowledgment.—We wish to thank Dr. R. Connor for his advice and assistance. The analyses were carried out under the direction of Dr. E. L. Stanley and Mr. C. W. Nash. Miss R. Lookabaugh carried out the preparation of a number of intermediates used in this work and Mr. H. J. Schneider performed the experiment on methylphenylacetylene.

Experimental

Phenylacetylene with Methyl and Ethyl Carbonates.—In a 1-liter, 3-necked flask equipped with a Hershberg stirrer, a dropping funnel and a soda lime tube there was prepared 0.5 mole of sodamide[4] in liquid ammonia. To the sodamide in liquid ammonia was added 51 g. (0.5 mole) of phenylacetylene, the ammonia allowed to evaporate at

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(1) For the first paper of this series, see Croxall and Schneider, THIS JOURNAL, **70**, 1257 (1948).

(2) Nightingale and Wadsworth, *ibid.*, **69**, 1183 (1947).

(3) Linstead, *J. Chem. Soc.*, 2503 (1929).

(4) Vaughn, Vogt and Nieuwland, THIS JOURNAL, **56**, 2121 (1934).

room temperature and the last traces removed at the water pump. The flask was then equipped with a reflux condenser topped with a soda lime tube and with vigorous stirring and cooling there was added 590 g. (5 moles) of ethyl carbonate. After the exothermic reaction had subsided, the mixture was heated to 80° and 204 g. (2 moles) of phenylacetylene was added over a one-hour period, the temperature being maintained at 70–80° by periodic cooling. After being heated for ten hours at 65–75°, the reaction mixture was cooled to room temperature and neutralized with 130 g. of aqueous 23% acetic acid. The oil layer was separated, washed with 200 ml. of water, dried over anhydrous potassium carbonate and distilled through a short packed column. After removal of ethanol and 265 g. of ethyl carbonate there was obtained (a) 75 g. of material b. p. 135° (2 mm.); n^{20}D 1.5202 and (b) 370 g. of material b. p. 135–148° (2 mm.); n^{20}D 1.5274. Both fractions *a* and *b* were carefully refractionated to give pure ethyl β-phenyl-β-ethoxyacrylate, b. p. 101–102.5° (0.4 mm.); n^{20}D 1.5320[5]; saponification equivalent 216 (calcd. 220) and ethyl β-phenyl-β,β-diethoxypropionate, b. p. 86–89° (0.24 mm.); n^{20}D 1.4920[6]; saponification equivalent 253 (calcd. 266). From the saponification equivalents, the combined fractions *a* and *b* correspond to 93% ethyl β-phenyl-β-ethoxyacrylate and 7% ethyl β-phenyl-β,β-diethoxypropionate. The yield of acrylate–propionate mixture was 73% based on the ethyl carbonate consumed, 80% on phenylacetylene and 400% on sodium.

In a similar experiment in which sodium ethoxide was substituted for sodium phenylacetylide, there was obtained 64% of the acrylate and 36% of the propionate. The yield was 46% based on the ethyl carbonate consumed, 76% on phenylacetylene and 152% on sodium ethoxide.

From a condensation reaction maintaned at 30–40°, methyl carbonate (1.9 moles), phenylacetylene (0.5 mole) and 0.2 mole of benzyltrimethylammonium methoxide (containing an equivalent of methanol)[1] there was obtained 38% methyl-β-phenyl-β-methoxyacrylate,[5,7] b. p. 101° (0.25 mm.); n^{20}D 1.5507; saponification equivalent 192 (calcd. 192) and 62% methyl β-phenyl-β,β-dimethoxypropionate,[6] b. p. 85–88° (1 mm.); n^{20}D 1.4997; saponification equivalent 213 (calcd. 224). The yield was 63% based on the methyl carbonate consumed, 80% on phenylacetylene and 208% on benzyltrimethylammonium methoxide.

2-Methyl-1-butene-3-yne with Ethyl Carbonate.—To 1.5 moles of sodium ethoxide and 1414 g. (12 moles) of ethyl carbonate in a 2-liter, 3-necked flask equipped with a dropping funnel, a gas-tight stainless steel stirrer whose blades scraped the bottom of the flask and a reflux condenser which was connected to an open end mercury manometer, there was added 204 g. (3.1 moles) of 2-methyl-1-butene-3-yne[8] over a period of four hours, the temperature being maintained at 70–80°. The mixture was heated at the above temperature six additional hours, cooled and neutralized with aqueous 23% acetic acid. Fractionation of the organic layer through a short packed column gave after removing ethanol and 866 g. (7.3 moles) of ethyl carbonate, (a) 189 g. of material, b. p. 73–80.5° (2 mm.); n^{20}D 1.4490–1.4527, 34 g. of an intermediate fraction, b. p. 80.5–100° (2 mm.) and (b) 216 g. (30%) of a constant boiling fraction, b. p. 100–103° (1 mm.); n^{20}D 1.4520, which proved to be 2-methyl-3,3-diethoxy-4-carbethoxy-1-butene (II). *Anal.* Calcd. for $C_{12}H_{22}O_4$: C, 62.58; H, 9.63. Found: C, 62.61; H, 9.53. There was also obtained 90 g. of a higher boiling material, b. p. 91–195° (1–4 mm.) which distilled with decomposition and was discarded.

In a similar experiment in which the condensation was carried out at 30–45°, there was obtained from 14 moles of ethyl carbonate, 3.8 moles of 2-methyl-1-butene-3-yne and 0.9 mole of benzyltrimethylammonium ethoxide (containing an equivalent of ethanol),[1] 1289 g. (10.9 moles) of unreacted ethyl carbonate, 289 g. of fraction *a*, 108 g. of fraction *b* and 170 g. of the high boiling fraction.

2-Methyl-3-ethoxy-4-carbethoxy-1,3-butadiene (I).—All attempts to fractionate cut *a* to obtain a pure compound were unsuccessful. However, by fractionating a toluene (100 g.) solution of fraction *a* (50 g.) in the presence of sodium bisulfate (0.25 g.) there was obtained 32 g. of an ethanol–toluene mixture, b. p. 76–110° (9.36% ethanol by hydroxyl determination) and 41 g. of the pure butadiene ester (I), b. p. 65–66° (1.7 mm.); n^{20}D 1.4690; saponification equivalent 185 (calcd. 190).

Anal. Calcd. for $C_{10}H_{16}O_3$: C, 65.18; H, 8.75. Found: C, 65.06; H, 8.74.

2-Methyl-3-ethoxy-4-carbethoxybutane (III).—In a high pressure hydrogenation bomb was placed 66 g. (0.36 mole) of (I) and 4 g. of Raney nickel. This mixture was treated with hydrogen at 1300 psi and 70–78° to give 56 g. of the butane ester (II), b. p. 81–81.5° (10 mm.); n^{20}D 1.4175; saponification equivalent 189 (calcd. 188).[3]

2-Methyl-3,3-diethoxy-4-carbethoxy-1-butene (II).—The pure butene ester (II) (fraction *b*) was characterized as follows. To 32 g. (0.14 mole) was added 23 ml. of aqueous 15% hydrochloric acid and 24 ml. of 95% ethanol. The mixture was allowed to stand ninety hours, refluxed for thirty minutes, cooled, neutralized with potassium carbonate, extracted with ether and dried over anhydrous potassium carbonate. After removing ether, fractionation gave 20 g. of an ethanol-water azeotrope, b. p. 76–78°, 14 g. of an intermediate fraction, b. p. 78–94° and 24 g. of crude methyl isopropenyl ketone, b. p. 94–99°. These last two fractions gave a semicarbazone which on recrystallization from ethanol-water melted at 173.5–175°. A mixed melting point with an authentic sample of the semicarbazone was 172.5–174°.

Fractionation of 30 g. (0.13 mole) of (II) and 50 g. of toluene in the presence of 0.5 g. of sodium bisulfate gave 11 g. of an ethanol–toluene fraction, b. p. 76–110° (98% yield of ethanol by hydroxyl determination) and 20 g. of the butadiene ester (I), b. p. 102° (12 mm.); n^{20}D 1.4688.

2-Methyl-3,3-diethoxy-4-carbethoxybutane (IV).—Hydrogenation of 40 g. (0.17 mole) of the butene ester (II) dissolved in 80 ml. of ethanol over 20 g. of Raney nickel at 1300 psi and 80° gave 31 g. of the butane ester (IV), b. p. 85–87° (1 mm.); n^{20}D 1.4308.

Anal. Calcd. for $C_{12}H_{24}O_4$: C, 62.04; H, 10.41. Found: C, 62.25; H, 10.38.

Acid hydrolysis of this ester gave methyl isopropyl ketone whose 2,4-dinitrophenylhydrazone melted at 116–117° and did not depress an authentic sample.

Summary

1. Phenylacetylene condenses with alkyl carbonates in the presence of basic condensation agents to produce alkyl β-phenyl-β-alkoxyacrylates ($C_6H_5C(OR){=}CHCO_2R$) and alkyl β-phenyl-β,β-dialkoxypropionates ($C_6H_5C(OR)_2CH_2CO_2R$).

2. 2-Methyl-1-butene-3-yne condenses with ethyl carbonate under similar conditions to give chiefly 2-methyl-3-ethoxy-4-carbethoxy-1,3-butadiene ($CH_2{=}C(CH_3)C(OC_2H_5){=}CHCO_2C_2H_5$) and 2-methyl-3,3-diethoxy-1-butene ($CH_2{=}C(CH_3)C(OC_2H_5)_2CH_2CO_2C_2H_5$).

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[5] Moureu, *Bull. soc. chim.*, [3] **31**, 509 (1904); see also ref. 7.

[6] Moureu, *ibid.*, [3] **31**, 493 (1904).

[7] v. Auwers, *Ann.*, **413**, 274 (1917).

[8] Carothers and Coffman, THIS JOURNAL, **54**, 4074 (1932).