equal molar amount of *tert*-butylhydrazine. Repeated washing with 1:1 benzene–pentane afforded a solid that was 85% pure (NMR): mp 90–92 °C dec; NMR ($CDCl_3$) 1.11 (s, *tert*-butylhydrazine) and 1.40 ppm (s, **7c**).

Anal. Calcd for $C_6H_{10}N_2O_3$: C, 45.57; H, 6.37; N, 17.71. Found: C, 46.17; H, 6.65; N, 18.69.

Acknowledgments. This work has been partially supported by the Alfred P. Sloan Research Foundation and the National Institutes of Health (GM 14518).

Registry No.—**3a**, 100-63-0; **3b**, 3178-39-0; **3c**, 32064-67-8; **4d**, 6233-02-9; **4e**, 40887-05-6; **4f**, 60103-93-7; **4g**, 60103-94-8; **5d**, 60103-95-9; **5e**, 60103-96-0; **5f**, 60103-97-1; **5g**, 60103-98-2; **6d**, 3711-77-1; **6e**, 60103-99-3; **6f**, 60104-00-9; **6g**, 60104-01-0; **7a**, 60104-02-1; **7b**, 60104-03-2; **7c**, 60104-04-3; benzyl chloroformate, 501-53-1; phosgene, 75-44-5; ethyldiisopropylamine, 7087-68-5; lithium diisopropylamide, 4111-54-0.

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(2) W. A. Henderson, Jr., and A. Zweig, *J. Chem. Soc., Chem. Commun.*, 169 (1972).

(3) Hurd and Cesark[1] proposed that a cyclization of this type might occur when the unsubstituted carbethoxyhydrazinecarbonyl chloride is pyrolyzed. However, no product from this type of cyclization was reported.

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New Syntheses of β,β-Dimethoxy Esters and Ketones by Conjugate Addition of Methanol to Some Activated Alkynes

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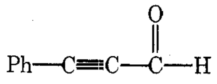
Received April 27, 1976

We have previously reported[2,3] that cyanide ion catalyzes the addition of the elements of one molecule of methanol to α,β-acetylenic aldehydes such as 3-phenyl-2-propynal (**1**), which yield a 1:1 mixture of *cis*- and *trans*-methyl 3-phenyl-2-propenoate (**2**). Others have also described[4,5] reactions of this type. A key step envisaged in the proposed[2] mechanism for this reaction is the prototropic shift of the aldehydic proton in the intermediate **3** (formed by nucleophilic attack of cyanide ion on the carbonyl group of **1**). A test of this mechanism might be made using α,β-acetylenic esters and ketones **4**, which possibly could provide the hydrocyanated product **5**. This report provides the answer to this query, at least for a few representative cases.

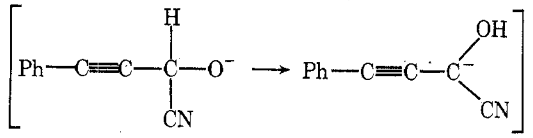


$$\mathrm{Ph-C\equiv C-\overset{\overset{O}{\|}}{C}-H}$$

1

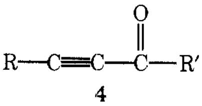
$$\mathrm{Ph-CH{=}CH-COOCH_3}$$

2



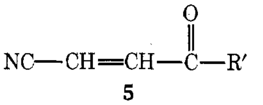
3

However, no product related to **5** was observed. Instead, the reaction of methyl 2-propynoate (**6**) with excess methanol using 1.2 molar equiv of sodium cyanide provided methyl 3,3-dimethoxypropanoate (**7**) as the major product (75%). When 0.1 molar equiv of sodium cyanide was used, a mixture was obtained that was predominantly ester **7** along with a lesser amount of methyl 3-methoxypropenoate (**8**). Relative yields were estimated from the infrared spectrum of the mixture. When the reaction was carried out in the presence of acetic acid, the ir spectrum of the crude reaction mixture showed the presence of a large amount of unsaturated ester **8** together with some ester **7**. The structure of ester **7** was established by comparison of boiling point and spectroscopic data with those of an authentic sample. Since the ester **7** is easily accessible by our method and has a potential aldehydic group present, it ought to be a useful bifunctional synthetic intermediate.



$$\mathrm{R-C\equiv C-\overset{\overset{O}{\|}}{C}-R'}$$

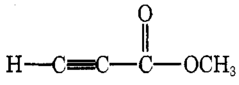
4



$$\mathrm{NC-CH{=}CH-\overset{\overset{O}{\|}}{C}-R'}$$

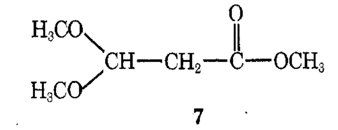
5

R′ = alkyl or alkoxy

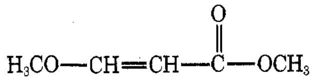


$$\mathrm{H-C\equiv C-\overset{\overset{O}{\|}}{C}-OCH_3}$$

6



7

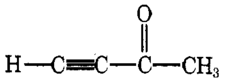


$$\mathrm{H_3CO-CH{=}CH-\overset{\overset{O}{\|}}{C}-OCH_3}$$

8

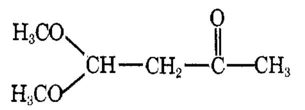
A possible mechanism for the conversion of ester **6** to **7** involves Michael addition of two molecules of methanol (presumably initiated by methoxide ion, generated by the reaction of sodium cyanide and methanol) in two steps via unsaturated ester **8**. The fact that olefinic ester **8** (prepared independently[6] by the reaction of **6** with methanol in the presence of triethylamine) on treatment with cyanide ion in methanol under these conditions also gives ester **7** supports the proposed mechanism.

It was of interest to investigate the extension of this reaction to α,β-acetylenic ketones. Treatment of commercially available 3-butyn-2-one (**9**) with 0.05 molar equiv of sodium cyanide in methanol at −10 °C for about 10 min gave 1,1-dimethoxy-3-butanone (**10**) in 88% yield; clearly, two molecules of methanol added to **9**. These reaction conditions are critical; increasing the amount of cyanide ion, temperature, and/or reaction time decreased the yield of **10**. The structure of ketone **10** was established by the identity of its ir spectrum with that of a commercial sample of 1,1-dimethoxy-3-butanone.



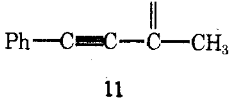
$$\mathrm{H-C\equiv C-\overset{\overset{O}{\|}}{C}-CH_3}$$

9



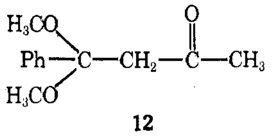
10

When the cyanide ion catalyzed addition reaction of methanol was carried out with 4-phenyl-3-butyn-2-one (**11**), a mixture of products was formed as indicated by the ir and NMR spectra of the crude product. Attempts to obtain a single product by variation of reaction conditions were not fruitful. It appeared that the nucleophilic nature of cyanide ion could have caused side reactions. We therefore tried next the poorly nucleophilic weak base, carbonate ion. It was gratifying to find that carbonate ion catalyzed addition of methanol to ketone **11** occurred smoothly at 0 °C to afford 1-phenyl-1,1-dimethoxy-3-butanone (**12**) in 86% yield. Expectedly, the carbonate ion also catalyzed the addition of methanol to methyl prop-2-ynoate (**6**), and 3-butyn-2-one (**9**)



$$\mathrm{Ph-C\equiv C-\overset{\overset{O}{\|}}{C}-CH_3}$$

11



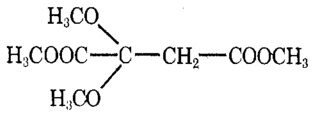
12

to afford ester **7** and ketone **10** in 74 and 84% yields, respectively.

The carbonate ion catalyzed addition of methanol to dimethyl acetylenedicarboxylate (**13**) gave a 5:1 mixture of esters **14** and **15a**. A 1:2.5 mixture of cis and trans esters **15a** and **15b**, prepared[6] by the triethylamine-catalyzed addition of methanol to **13**, on carbonate ion catalyzed addition of methanol gave results similar to those obtained with the acetylenic ester **13**. This further supports the mechanism suggested above.

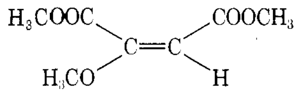
$H_3COOC{-}C{\equiv}C{-}COOCH_3$

13

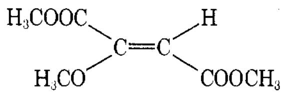


$H_3COOC{-}C(OCH_3)_2{-}CH_2{-}COOCH_3$

14



15a



15b

Experimental Section

General. Boiling points are uncorrected. Infrared spectra were taken in chloroform solution, unless otherwise noted, with a Perkin-Elmer Model 237 infrared spectrophotometer. The NMR spectra were recorded on a Varian A-60 in chloroform-*d* solution with tetramethylsilane as the internal standard. Chemical shifts are reported in parts per million (δ) and signals are described as s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet).

Methyl 3,3-Dimethoxypropanoate (7). Method A. Cyanide Ion Catalyst. To a magnetically stirred ice-cooled solution of 8.4 g (0.1 mol) of methyl 2-propynoate (**6**) in methanol (100 ml) was added 6.4 g (0.13 mol) of sodium cyanide in 100 ml of methanol over a period of 15 min. The solution, which developed a light yellow color, was stirred at ambient temperature (about 23 °C) for 48 h. After most of the methanol was evaporated on a steam bath, the residue was diluted with ice–water, when oily globules separated. The oil was extracted with ether, and the ethereal layer washed twice with brine, dried over anhydrous Na_2SO_4, and concentrated to afford 11.1 g (75%) of crude yellow oil. Fractional distillation provided analytically pure methyl 3,3-dimethoxypropanoate (**7**): bp 79–80 °c)25 Torr) [lit.[7] bp 77 °C (20 Torr)]; ir (CCl_4) 1745 (saturated ester), 1130 (ether), transparent 2100–2300 cm^{-1} (absence of triple bond); NMR ($CDCl_3$) δ 2.67 (d, 2 H of CH_2, $J = 6$ Hz), 3.38 (s, 6 H of OCH_3), 3.75 (s, 3H of $-OCH_3$), 4.88 (t, 1 H of -CH, $J = 6$ Hz).

Method B. Carbonate Ion Catalyst. To a magnetically stirred, cooled solution (−5 to −6 °C) of 0.84 g (0.01 mol) of methyl 2-propynoate (**6**) in 12 ml of methanol was added a suspension of 0.41 g (0.003 mol) of potassium carbonate in 12 ml of methanol. After the addition no significant change in color was noticed. The solution was stirred at that temperature for an additional 24 h. The undissolved carbonate was filtered, methanol removed by heating, and the organic material extracted with ether. The dried (Na_2SO_4) ethereal extract after concentration and distillation gave 1.03 g (70%) of methyl 3,3-dimethoxypropanoate (**7**), bp 72–73 °C (18.5 Torr).

Conversion of methyl 3-methoxy-2-propenoate (8)[6] to methyl 3,3-dimethoxypropanoate (7) was carried out using conditions similar to those described above in method A. The usual workup gave crude methyl 3,3-dimethoxypropanoate (**7**) (62%) as a yellow-brown oil, the ir and NMR spectra of which were almost identical with those of pure ester **7**.

1,1-Dimethoxy-3-butanone (10). Method A. Cyanide Ion Catalyst. To a cooled (−10 °C) solution of 3-butyn-2-one (**9**, 1.36 g, 0.02 mol) in 15 ml of methanol was added dropwise a solution (0.049 g, 0.001 mol) of sodium cyanide in 8 ml of methanol. After the addition the solution developed a light yellow color and stirring was continued for an additional 8 min when the solution developed a light red color. Methanol was removed by heating, the residue extracted with ether, and the ethereal layer washed with brine, dried (Na_2SO_4), and concentrated to give 2.3 g (88%) of 1,1-dimethoxy-3-butanone (**10**). Fractional distillation gave 2.1 g (79%) of 1,1-dimethoxy-3-butanone (**10**): bp 67 °C (18 Torr) [lit.[8] bp 38 °C (2 Torr)]; ir (CCl_4) 1720 (C=O), transparent from 2100 to 2250 cm^{-1} (absence of triple bond); NMR ($CDCl_3$) δ 2.18 (s, 3 H of CH_3), 2.76 (2.18–2.71, d, 2 H of CH_2), 3.40 (s, 6 H of 2 OCH_3), and 4.86 (t, 1 H of CH). The structure was established by the superimposability of its ir spectrum on that of an authentic sample.

Method B. Carbonate Ion Catalyst. A suspension of 0.69 g (0.005 mol) of potassium carbonate in 75 ml of methanol was added to an ice-cooled solution of 3-butyn-2-one (6.8 g, 0.1 mol) in 75 ml of methanol. After a period of 15 min when the solution was very light yellow in color most of the methanol was removed on steam bath. The product was extracted with ether, and the ethereal layer washed with brine, dried over anhydrous sodium sulfate, and concentrated to afford 11.1 g (84%) of pale yellow oil. Fractional distillation gave pure product, bp 72 °C (19 Torr), the ir and NMR spectra of which were identical with those of ester **10** obtained by method A.

Reaction of 4-Phenyl-3-butyn-2-one (11) with Methanol in the Presence of Potassium Carbonate. To an ice-cooled solution of 2.88 g (0.02 mol) of 4-phenyl-3-butyn-2-one (**11**) in 30 ml of methanol was added 2.76 g (0.02 mol) of potassium carbonate in 30 ml of methanol over a period of 10 min; a deep yellow color developed. The solution was stirred in ice water for an additional 40 min; the color changed to yellowish red. The usual workup gave 3.69 g (89%) of reddish yellow oil, which upon fractional distillation afforded 3.08 g (77%) of 1,1-dimethoxy-1-phenyl-3-butanone (**12**): bp 90–96 °C (2 Torr); ir (CCl_4) 1710 cm^{-1} (ketone); NMR ($CDCl_3$) δ 1.68 (s, 3 H, CH_3 of $COCH_3$), 3.17 (s, 6 H, 2-CH_3 of OCH_3), 3.05 (s, 2 H of CH_2), and 7.40 (m, 5 H of phenyl).

Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.62; H, 7.54.

Reaction of Dimethyl Acetylenedicarboxylate (13) with Methanol in the Presence of Potassium Carbonate. To a solution of potassium carbonate (0.41 g, 0.003 mol) in 40 ml of methanol was added a solution of 4.26 g (0.03 mol) of dimethyl acetylenedicarboxylate in 40 ml of methanol over a period of 15 min at room temperature. After the mixture was stirred for 5 h, methanol was removed, the residue taken up in ether, and the ethereal layer washed twice with brine, dried over anhydrous sodium sulfate, and evaporated, leaving 4.85 g of light yellow liquid, which was fractionally distilled to yield 4.25 g of an oil: bp 129 °C (13 Torr); ir ($CHCl_3$) 1750 (s, -COOR), 1720 (m, unsaturated ester), 1620 (s, olefinic), and 1145 cm^{-1} (s, ether); NMR ($CDCl_3$) δ 3.0 (s, 2 H of $-CH_2$), 3.3 (s, 2 CH_3 of OCH_3), 3.68 (s, CH_3 of $COOCH_3$), and 5.28 (s, 1 H of CH). The value at δ 5.28 is assigned[6] to the olefinic proton in cis ester **15a**, while the signal at δ 3.0 is assigned to the methylene proton in methyl 3,3-dimethoxy-3-carbomethoxypropanoate (**14**). Integration showed the two esters **15a** and **14** to be present in the ratio of 1:5.

Reaction of Methyl *cis*- and *trans*-3-Methoxy-3-carbomethoxy-2-propenoate (15a and 15b)[6] with Methanol in the Presence of Potassium Carbonate. A solution of cis and trans esters **15a** and **15b** (4.35 g, 0.025 mol) was subjected to dropwise addition of potassium carbonate solution (0.33 g, 0.0025 mol in 40 ml of methanol) at room temperature. The resulting mixture was stirred for an additional 5 h. The usual workup gave 4.38 g of colorless, oily material which was fractionally distilled to yield 4.0 g of material, bp 128–129 °C (13 Torr). The ir and NMR spectra for this material were identical with those obtained above in the reaction of dimethyl acetylenedicarboxylate with methanol.

Acknowledgments. We thank Mr. Gordon G. Boudreaux, Southern Regional Research Laboratory, U.S. Department of Agriculture, for NMR spectra.

Registry No.—**6**, 922-67-8; **7**, 7424-91-1; **8**, 34846-90-7; **9**, 1423-60-5; **10**, 5436-21-5; **11**, 1817-57-8; **12**, 60084-52-8; **13**, 762-42-5; **14**, 2215-04-5; **15a**, 2509-14-0; **15b**, 2215-05-6; methanol, 67-56-1.

References and Notes

(1) This paper is abstracted from part of the Ph.D. Dissertation of Amrik Singh Walia, Loyola University, New Orleans, 1975.
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