The Reaction of *cis*- and *trans*-1,2-Dimethoxy-1-chloroethylenes with Alkyllithium Reagents

B. R. O'Connor

Contribution No. 1334 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

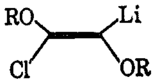
Received August 22, 1967

cis- and *trans*-1,2-dimethoxy-1-chloroethylene have been prepared and treated with *n*- and *sec*-butyllithium at low temperatures. The major product from both isomers was an amorphous solid of composition $(C_4H_6O_2)_n$. Trapping experiments indicate that the α-alkoxyvinyllithium compounds **5a** and **5b** were intermediates in the reaction, and that significant concentrations of dimethoxyacetylene may have been formed by elimination of lithium chloride from **5a**.

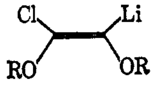
Bis(aryloxy)- and bis(alkoxy)ethynes, ROC≡COR, have not been described[1] although the corresponding bis(alkylthio)- and bis(dialkylamino)ethynes are known.[2]

A number of unsuccessful attempts to synthesize bis(alkoxy)ethynes have been reported. McElvain and Stammer found[3] that 1-bromo-1,2-diethoxyethylene was resistant to dehydrobromination by potassium *t*-butoxide and that it reacted with *n*-butyllithium in ether at −35° to form a lithium compound which upon protonation with ethanol gave 1,2-diethoxyethylene. Baganz and Krüger[4] reported that 1,2-dichloro-1,2-di-*n*-butoxyethylene did not react with zinc in methanol, but did react with sodium in ether, sodium butoxide and sodium acetylide being the only identified products. Alkylation of potassium acetylenediolate with *n*-butyl bromide followed by hydrolysis gave *dl*-α-hydroxycaproic acid, and with methyl iodide a yellow liquid having the composition $C_8H_{12}O_4$ was obtained.[5,6] There was no evidence of the formation of a bis(alkoxy)ethyne.

The recent reports of Köbrich and Flory[7] that several α-chlorovinyllithium compounds were prepared and were moderately stable in ether solvents at low temperatures suggested that the α-alkoxyvinyllithium compounds **1a** and **1b** might also be stable under similar conditions. If lithium chloride could then be eliminated from these compounds at higher temperatures, bis(alkoxy)ethynes would be formed under relatively mild conditions in the absence of strong nucleophiles. Köbrich has reviewed this type of elimination reaction from olefins.[8]



1a



1b

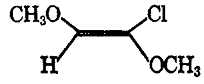
We wish to report the results of our investigation of the reactions of *trans*- and *cis*-1,2-dimethoxy-1-chloroethylene **2a** and **2b** with alkyllithium reagents.

Results

trans- and *cis*-1,2-dimethoxy-1-chloroethylene **2a** and **2b** were synthesized by chlorinating a mixture of *cis*- and *trans*-1,2-dimethoxyethylene[9] and dehydrochlorinating the resulting 1,2-dichloro-1,2-dimethoxyethane.[10] 1,2-Dimethoxy-1-chloroethylene (2) was obtained as a mixture of isomers, bp 132° (isomer X) and 139° (isomer Y), which were separated by gas chromatography. Mixtures rich in either isomer were obtained by dehydrochlorinating the *meso* and *dl* forms of 1,2-dimethoxy-1,2-dichloroethane, which could be partially separated.

A structural assignment for the isomers can be made from the nmr and reactivity data. The chemical shifts of the olefinic protons of *cis*- and *trans*-1,2-dichloroethylene differed by less than 0.1 ppm,[11] whereas the olefinic protons of *trans*-1,2-dimethoxyethylene were shifted 0.92 ppm downfield from the olefinic protons of the *cis* isomer. These data suggest that the 1,2-dimethoxy-1-chloroethylene isomer ($\tau_X - \tau_Y = 0.55$ ppm) with its olefinic proton shifted to lower field (isomer Y) has *trans*-methoxyl groups. A second feature of the nmr spectra supported this assignment. Isomer X had two singlets in the methoxyl proton region (differing in chemical shift by 0.06 ppm), whereas isomer Y had only one. *cis*-1,2-Dimethoxy-1-chloroethylene might reasonably show two sets of methoxyl protons in the nmr spectrum since one methoxyl group is flanked by a C–H and a C–O bond and the second by a C–Cl and a C–O bond. In the *trans* isomer both methoxyl groups are flanked by a C–H and a C–Cl bond.

The relative reactivity of the isomers with potassium hydroxide lent further support to the assignment. β-Halovinyl ethers eliminate smoothly with oxygen bases only when hydrogen and halogen are arranged *trans* to each other.[3] Since isomer Y reacted readily with potassium hydroxide and isomer X did not, isomer Y can be assigned a *trans* arrangement of the hydrogen and chlorine atoms. Therefore, isomer X is *cis*-1,2-dimethoxy-1-chloroethylene **2b** and isomer Y is *trans*-1,2-dimethoxy-1-chloroethylene, **2a**.



2a

2b

---

[1] For a review of ethynyl ethers and thio ethers, see J. F. Arens, "Advances in Organic Chemistry, Methods and Results," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1960, pp 117–212.

[2] H. G. Viehe and M. Reinstein, *Angew. Chem.*, **76**, 537 (1964); H. G. Viehe, *Angew. Chem. Intern. Ed. Engl.*, **6**, 767 (1967).

[3] S. M. McElvain and C. H. Stammer, *J. Amer. Chem. Soc.*, **75**, 2154 (1953).

[4] H. Baganz and K. E. Krüger, *Chem. Ber.*, **87**, 1622 (1954).

[5] W. Büchner, *Helv. Chim. Acta.*, **46**, 2111 (1963).

[6] W. F. Sager, A. Fatiadi, P. C. Parks, D. B. White, and T. P. Perros, *J. Inorg. Nucl. Chem.*, **25**, 187 (1963).

[7] G. Köbrich and K. Flory, *Tetrahedron Lett.*, 1137 (1964); *Chem. Ber.*, **99**, 1773 (1966).

[8] G. Köbrich, *Angew. Chem. Intern. Ed. Engl.*, **4**, 49 (1965).

[9] W. F. Gresham, *Chem. Abstr.*, **45**, 1620*i* (1951); H. Baganz, K. Praefcke, and J. Rost, *Chem. Ber.*, **96**, 2657 (1963); R. C. Schreyer, *J. Amer. Chem. Soc.*, **73**, 2962 (1951).

[10] H. Baganz and R. F. Krüger, *Chem. Ber.*, **87**, 1622 (1954).

[11] Varian High Resolution NMR Spectra Catalogue, Name Index No. 154 and 155.

When one equivalent of *n*-butyllithium was added to a solution of *trans*-1,2-dimethoxy-1-chloroethylene in tetrahydrofuran–hexane at −100°, reaction occurred and the *trans* isomer was completely consumed. The *cis* isomer reacted much more slowly, and in competition experiments the *trans* isomer reacted completely before any of the *cis* isomer had reacted.[12]

A white solid was formed in the reactions of *n*-butyllithium with the *trans* isomer **2a** at −100°; between −70 and −60° it dissolved and between −50 and −40° another solid sometimes precipitated. This latter product was obtained as a pale yellow, amorphous powder of composition $(C_4H_6O_2)_n$. The yield was 70–80% of the maximum calculated on the basis of the amount of **2a** consumed. In other experiments little or no material precipitated at the higher temperature, but work-up yielded oils from which low yields (10–20%) of amorphous solids with compositions close to $(C_4H_6O_2)_n$ were obtained.

Methyl methoxyacetate was formed (50–80% yield) when dilute aqueous acid was added to a reaction of **2a** with *n*-butyllithium at −100°, and some **2a** (but no **2b**) was recovered. Gas chromatographic analysis of the mixture before the acid was added indicated all the **2a** had reacted and no methyl methoxyacetate was present. Control experiments established that *cis*- and *trans*-1,2-dimethoxy-1-chloroethylene did not react with dilute acid under these conditions and that methyl methoxyacetate, if formed before the addition of dilute acid, would survive and be detected.

When an ether solution of anhydrous hydrogen chloride was added to a reaction solution of *n*-butyllithium and **2a** which had warmed to −30° without precipitating a solid product, **2a** was regenerated (50% yield) and no **2b** was formed. When the addition was made at 0°, 10–15% of **2a** was reformed (no **2b**), and making the addition at 25° yielded no **2a** or **2b**. Neither isomer underwent reaction with hydrogen chloride under these conditions.

cis-1,2-Dimethoxy-1-chloroethylene **2b** was allowed to react rapidly with *sec*-butyllithium in tetrahydrofuran–hexane at −100°, and at between −60 and −50° a pale yellow solid always precipitated. This product, which had properties similar to those of the amorphous material obtained from some reactions of **2a** with *n*-butyllithium, had the composition $(C_4H_6O_2)_n$ and was obtained in about 60% yield. Addition of excess dilute acid to a reaction mixture of **2b** and *sec*-butyllithium after 30 min at −100° regenerated 40% of **2b** which had reacted. No **2a** and no methyl methoxyacetate were detected in the mixture after acidolysis. A small amount (*ca.* 5%) of the ester was detected and about 40% of **2b** was regenerated after acidolysis of a reaction mixture which had warmed to −75°.

When an ether solution (at −80°) of anhydrous hydrogen chloride was added to a reaction mixture of **2b** and *sec*-butyllithium after 4 hr at −100°, **2b** was recovered in nearly quantitative yield, and no **2a** was detected. Addition of the hydrogen chloride solution to a reaction mixture which had been at −100° for 2 hr, then at −80° for 2 hr, resulted in recovery of about 75% of the **2b** and no **2a** was formed. However, when a reaction mixture held at −80° for 5 hr (or warmed to −70° over a shorter period of time) was quenched with ethereal hydrogen chloride, none of the reacted **2b** was regenerated and small amounts (*ca.* 5%) of the *trans* isomer could be detected.

When excess carbon dioxide was added to a reaction of **2b** with *sec*-butyllithium at −100°, an isomer of 2,3-dimethoxy-3-chloroacrylic acid **3** was obtained. The yield of **3** (about 45%) was not significantly dependent upon the reaction period at −100° (5 or 100 min). Rapid carbonation of reaction mixtures from **2a** and *n*-butyllithium did not yield **3**. The acidic products included small amounts of valeric acid and an oil tentatively identified from nmr spectra as a mixture of isomers of 3-butyl-2,3-dimethoxyacrylic acid, **4**.

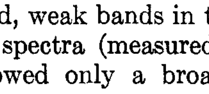
$$\underset{\mathbf{3}}{CH_3OC(Cl){=}C(OCH_3)CO_2H} \qquad \underset{\mathbf{4}}{n\text{-}C_4H_9C(OCH_3){=}C(OCH_3)CO_2H}$$

Finally, two related routes to dimethoxyacetylene were investigated briefly. Thermolysis of the silver salt of **3** neat or in refluxing acetonitrile yielded metallic silver and no gas was evolved. Thermolysis of bis-(2-chloro-1,2-dimethoxyvinyl)mercury, obtained by adding mercuric chloride to a reaction of **2b** and *sec*-butyllithium at −100°, yielded mercury and little or no mercuric chloride.

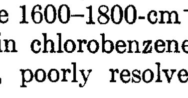
Discussion

The amorphous solids formed in the reactions of **2a** and **2b** with *n*-butyllithium and *sec*-butyllithium, respectively, appeared to be oligomers of dimethoxyacetylene. They analyzed correctly for $C_4H_6O_2$ and contained, at most, only trace amounts of chlorine. The infrared spectra had a sharp band at 2820–2830 cm^{-1} characteristic of the methoxyl group[13] and very strong bands in the carbon–oxygen stretching region. There were very broad, weak bands in the 1600–1800-cm^{-1} region. The nmr spectra (measured in chlorobenzene at 115–125°) showed only a broad, poorly resolved, signal centered at τ 6.1 ppm.

The possibility that dimethoxyacetylene was being formed as an intermediate in these reactions was investigated briefly. Our results indicate that the lithium compounds[14] **5a** and **5b** are formed rapidly in the reactions of *n*-butyllithium with **2a** and *sec*-butyllithium with **2b**, respectively, at −100° in tetrahydrofuran–hexane. The lithium compound **5a** could be trapped in low yield with aqueous acid or cyclopentadiene, but not by carbon dioxide. The compound **5b** appeared to be more stable and could be trapped in good yield by a variety of electrophiles (CO_2, $HgCl_2$, H_3O^+, HCl). The difference in stability between **5a** and **5b** was not unexpected since Kobrich has reported several examples of lithium compounds in which the *cis* arrangement of lith-



5a



5b

---

[12] In diethyl ether–hexane solution neither isomer had reacted after 4 hr at −100°.

[13] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, p 16.

[14] The state of aggregation of the lithium compounds cannot be specified.

ium and chlorine is more stable than the *trans* arrangement.[7,15,16]

The formation of methyl methoxyacetate (20–85%, depending upon the temperature), when excess dilute acid was added to reaction mixtures, from **2a** lent support to the idea that dimethoxyacetylene was an intermediate in the reaction, since monoalkoxyacetylenes react rapidly with dilute acid according to eq 1 and dimethoxyacetylene would be expected to yield methyl methoxyacetate ($R = OCH_3$, $R' = CH_3$).[1] Furthermore, the reformation of **2a** when anhydrous hydrogen chloride was added to reaction mixtures from **2a** at 0° or −30° suggests that dimethoxyacetylene was present. All our data indicate that the lithium compound **5a** must be completely decomposed at these temperatures, so it seems likely that hydrogen chloride added exclusively *trans* to dimethoxyacetylene to reform **2a**. Alkoxyacetylenes have been reported to react rapidly with anhydrous hydrogen halides in ethereal solvents.[1]

$$RC{\equiv}COR' + H_3O^+ \longrightarrow RCH_2CO_2R' \qquad (1)$$

Attempts to trap dimethoxyacetylene generated from **2a** at low temperatures with cyclopentadiene, diphenylisobenzofuran, tetraphenylcyclopentadienone, 3,4-dicyanofuran, tetracyanoethylene, or dimethylacetylene dicarboxylate were unsuccessful.

Although the *cis* olefin **2b** was allowed to react with *sec*-butyllithium to yield oligomers of dimethoxyacetylene, we were unable to trap any significant amount of dimethoxyacetylene with aqueous acid or anhydrous hydrogen chloride. At the temperature **5b** decomposed to yield dimethoxyacetylene, the rate of the oligomerization reaction may have been sufficient to prevent a buildup in concentration of the intermediate.

There are many aspects of the reaction of **2a** and **2b** with alkyllithium reagents such as the difference in reactivity between **2a** and **2b** with *n*-butyllithium, the effect of solvent, the mechanism of the decomposition of **5a** and **5b** (*via* **5a**?) and the mechanism of oligomerization of dimethoxyacetylene, which we have not investigated. However, we believe that our data, taken as a whole, do support the suggestion that, at low temperatures, dilute solutions of dimethoxyacetylene are formed from the reaction of **2a** and *n*-butyllithium in tetrahydrofuran–hexane.

Experimental Section

Melting points and boiling points are uncorrected. Infrared, nmr, ultraviolet, and mass spectra were determined on Perkin-Elmer Model 21, Varian A-60, Cary Model 14, and CEC-21-103C spectrometers, respectively.

Gas chromatographic analyses were made using a 6 ft × 0.25 in. column packed with Dow Corning FS-12-65 fluid 20% on Gas Chrom A operated at 85° with a helium flow of 65 cc/min unless indicated otherwise.

1,2-Dimethoxyethylene.[9]—1,1,2-Trimethoxyethane (250 g, 2.1 mol, Aldrich) was passed through a 2 ft × 1 in. vertical column packed with 10 mesh silica gel (Davidson No. 70 grade) which had been dried at 280° for 2 hr in a stream of nitrogen. The trimethoxyethane was added dropwise under nitrogen (60 cc/min) at a rate of 40 ml/hr to the column, which was maintained at 280–300°. The products were collected in a 500-ml flask attached to the column and cooled in a Dry Ice–isopropyl alcohol bath. The product mixture was poured into 250 ml of a 5% sodium carbonate solution and extracted with three 150-ml portions of ether. The extracts were dried over anhydrous potassium carbonate and distilled through a 12-in. Vigreux column. 1,2-Dimethoxyethylene was obtained as 100 g (54% yield) of a mixture of isomers: bp 98–102°, $n^{25}{}_D$ 1.4174 (lit.[9] for *cis* isomer, bp 97°, $n^{25}{}_D$ 1.4190; for *trans* isomer, bp 93°, $n^{25}{}_D$ 1.4070).

The nmr spectrum of the 98–102° mixture showed the higher boiling isomer (88%) to have singlets at τ 5.1 (1 H) and 6.84 (3 H). The nmr spectrum of a mixture (bp 90–95°) rich in the lower boiling isomer showed it to have singlets at τ 4.08 (1 H) and 6.93 (3 H).

1,2-Dimethoxy-1-chloroethylene.—Chlorine gas was passed through phosphorus pentoxide and bubbled slowly into 100 g (1.15 mol) of dimethoxyethylene (*ca.* 90:10 *cis/trans*), cooled in a Dry Ice–carbon tetrachloride bath, until the yellow color of excess chlorine persisted (*ca.* 1.2 mol). The crude 1,2-dichloro-1,2-dimethoxyethane[9] was dissolved in 200 ml of benzene, and the solution was added rapidly to a slurry of 150 g (86%, 2.3 mol) of powdered potassium hydroxide in 200 ml of cyclohexane.[10] During the addition the temperature rose to 65°. The reaction mixture was stirred overnight at 25° and was then heated at 50–60° for 1 hr. The insoluble salts were collected and washed thoroughly with benzene; the filtrate was washed once with water and dried over potassium carbonate. The benzene and cyclohexane were removed in an 18-in. spinning-band (Pt band) column at 760 mm, and the 1,2-dimethoxy-1-chloroethylene was obtained as 79 g (50% yield) of a mixture of isomers (52% *cis*, 48% *trans*) with bp 68–72° (66 mm) and 132–144° (760 mm). In another experiment a fraction with bp 138–139° (760 mm) was collected.

Anal. Calcd for $C_4H_7O_2Cl$: C, 39.22; H, 5.76; Cl, 28.95. Found: C, 39.23; H, 5.77; Cl, 28.70.

The two isomers were separated on a preparative scale with a 6-ft 25% fluorosilicone column at 85° with a helium flow rate of 350 cc/min.

The lower boiling isomer had the following spectral data: nmr (neat), τ 4.47 (s, 1), 6.56 (s, 3), 6.62 (s, 3); ir (neat), 1684 cm^{-1}; mass spectrum, *m/e* (relative intensity), 124 (0.13), 122 (0.39).

Anal. Found: C, 38.70; H, 5.82; Cl, 28.91.

The higher boiling isomer had the following spectral data: nmr (neat), τ 3.92 (s, 1), 6.61 (s, 6); ir (neat), 1690 cm^{-1}; mass spectrum, *m/e* (relative intensity), 124 (0.11), 122 (0.30).

Anal. Found: C, 38.92; H, 5.81; Cl, 28.49.

Mixtures rich in either isomer were obtained by separating the isomers of 1,2-dichloro-1,2-dimethoxyethane. A solid isomer, mp 68–71° (lit.[17] for 1,2-dichloro-1,2-dimethoxyethane, mp 72°, isomer not specified), was obtained by filtering the crude chlorination product, and this isomer upon dehydrochlorination with powdered potassium hydroxide yielded mixtures rich in the lower boiling isomer of 1,2-dimethoxy-1-chloroethylene.

A liquid isomer of 1,2-dichloro-1,2-dimethoxyethane (contaminated by about 25% dissolved solid isomer) yielded mixtures rich in the higher boiling isomer of 1,2-dimethoxy-1-chloroethylene upon dehydrochlorination under the same conditions.

Reactions of *trans*-1,2-Dimethoxy-1-chloroethylene with *n*-Butyllithium. A.—To a solution of 1.8 g (0.015 mol) of *trans*-1,2-dimethoxy-1-chloroethylene (contaminated by 5% *cis* isomer) in 50 ml of anhydrous THF (containing 0.5 ml of toluene as an internal standard) cooled to −100° under nitrogen was added dropwise over 15 min 8.5 ml (0.014 mol) of a 1.6 *M* solution of *n*-butyllithium in hexane (Foote) at 25°. After 30 min at −100° a small aliquot was withdrawn and quenched with Dry Ice. Vapor phase chromatographic analysis of the aliquot indicated that about 95% of the *trans* isomer and 0% of the *cis* isomer had reacted, and there was no component present with the retention time of authentic methyl methoxyacetate. A second aliquot quenched with a mixture of 0.5 *N* hydrochloric acid and Dry Ice showed the same amounts of *trans* and *cis* olefins and a significant amount of a component with the retention time of methyl methoxyacetate. After a total of 115 min at −100° the reaction mixture was cloudy and colorless. As the mixture warmed, a yellow color developed, and between −90 and −60° the solution was bright yellow and clear. A solid formed rapidly at −50 to −40°. At −20° an aliquot, hydrolyzed with dilute acid as above, showed only a trace of the ester.

---

[15] Our results also suggest there is a preference for elimination of lithium chloride rather than lithium methoxide in **5a** and **5b**. A similar observation has been made by Normant.[16]

[16] J. Normant, *Bull. Soc. Chim. Fr.*, 1876 (1963).

[17] H. Fiesselmann and F. Hörndler, *Chem. Ber.*, **87**, 911 (1954).

At 25° 1.2 g of a pale yellow solid was collected, washed with water and ethanol, and dried at 100° (0.5 mm) for 15 hr to yield 1.0 g (*ca.* 80%) of a pale yellow amorphous solid: mp 230–240° dec; ir (KBr), 2930 (m), 2829 (m), 1750 (w), 1645 (w), 1460 (m), 1235 (vs), 1208 (vs), 1143 (vs), 950 (m), 728 (w), and 705 (w) cm^{-1}; nmr (chlorobenzene at 115°), τ 6.1 ppm (broad singlet).

Anal. Calcd for $C_4H_6O_2$: C, 55.80; H, 7.02. Found: C 55.57; H, 7.11; Cl, 0.0 (Beilstein test).

B.—The reaction was repeated using 0.041 mol of *trans* olefin and 0.041 mol of *n*-butyllithium solution in 150 ml of tetrahydrofuran–hexane. The mixture was warmed to 25° after the butyllithium addition was complete, and no insoluble product was formed. Vapor phase chromatographic analysis indicated that 100% of the *trans* isomer had reacted. The solution was washed with dilute acid, and the aqueous wash was back extracted with ether. The combined extracts and organic layer were dried and concentrated under reduced pressure leaving a yellow-orange semisolid. Trituration with hexane yielded 0.5 g (15%) of a pale yellow solid: mp 90–135°; ir (KBr), 2950 (m), 2850 (w), 1750 (m), 1645 (w), 1300–1205 (s), 1145 (s), and 950 cm^{-1} (m); nmr ($CDCl_3$), τ 6.4 ppm (broad singlet).

Anal. Found: C, 53.67, 54.01; H, 7.08; 7.17; Cl, 0.0 (Beilstein test).

The filtrate yielded a yellow semisolid (3.0 g) which had a broad multiplet centered at τ 6.4–6.5 in the nmr spectrum and weaker multiplets at τ 7.6, 8.6, and 9.1, characteristic of *n*-butyl residues.

C.—When 1 equiv of *n*-butyllithium was added to a 65:35 mixture of *cis–trans* isomers in anhydrous ether at −100°, neither isomer reacted after 4 hr at −100°. The mixture was carbonated at −100°, and the starting olefins were recovered.

Reactions of *cis*-1,2-Dimethoxy-1-chloroethylene with Butyllithium Reagents. A. *n*-Butyllithium.—To a dilute solution of *cis*-1,2-dimethoxy-1-chloroethylene in tetrahydrofuran at −100° was added rapidly 1 equiv of *n*-butyllithium in hexane solution. As the reaction mixture warmed slowly, aliquots were withdrawn, quenched with Dry Ice, and analyzed by gc. At −80° 18% of the *cis* isomer had reacted, 60% had reacted at −60°, and 85% had reacted at +10°. The products were not identified.

B. *sec*-Butyllithium.—To a solution of 3.8 g (0.031 mol) of *cis*-1,2-dimethoxy-1-chloroethylene in 100 ml of anhydrous tetrahydrofuran at −110° was added over a 10-min period 20 ml (0.032 mol) of *sec*-butyllithium in hexane (Foote Mineral). Gc analysis indicated all the *cis* isomer had reacted. The mixture was warmed and at −80° the white solids present dissolved; at −50° a new yellow solid formed rapidly. At 25° the solid was collected and digested with water. The water-insoluble product was obtained at 1.5 g (60%) of an amorphous yellow solid: mp 210–245° dec; ir (KBr), 2930 (m), 2829 (m), 1750 (w), 1645 (w), 1460 (m), 1235 (vs), 1208 (vs), 1141 (vs), 950 (m), 728 (w), and 705 (w) cm^{-1}; nmr (chlorobenzene at 115°), τ 6.1 ppm (broad singlet).

Anal. Calcd for $C_4H_6O_2$: C, 55.80; H, 7.02. Found: C, 55.48; H, 7.06; Cl, 0.24.

When the experiment was repeated using 0.036 mol of **2b** and 0.039 mol of *sec*-butyllithium, 75% of **2b** reacted and 1.4 g (60% yield) of amorphous polymer, mp 210–250° dec, was obtained.

Dimethoxyacetylene Trapping Experiments. A. Dilute Acid.—To a solution of 1.8 g (0.015 mol) of *trans*-1,2-dimethoxy-1-chloroethylene (contaminated by 5% *cis*) in 50 ml of anhydrous tetrahydrofuran (containing 0.5 ml of toluene as an internal standard) cooled to −100° under nitrogen was added dropwise over 20 min 8.5 ml of a 1.6 *M* solution (*ca.* 0.014 mol) of *n*-butyllithium in hexane at 25°. The reaction mixture was stirred at −100 to −110° for 30 min and then an aliquot was withdrawn and quenched with Dry Ice. Vapor phase chromatographic analysis indicated that 95% of the *trans* isomer and 0% of the *cis* had reacted, and there was no component with the retention time of methyl methoxyacetate. Excess (20 ml of 0.5 *N*) hydrochloric acid solution was added dropwise at −100° and the mixture was warmed to 25°. The organic layer was separated, and the aqueous layer extracted with methylene chloride. The combined organic solutions were dried and concentrated, leaving 1.1 g of a yellow oil. Gc analysis[18] (using toluene and *cis*-1,2-dimethoxyethylene as internal standards) indicated 47% of the maximum amount of ester based on reacted *trans* olefin had been obtained. The nmr spectrum confirmed the presence of methyl methoxyacetate and a 50% yield of the ester, using toluene and *cis* isomer as internal standards, was indicated.

In similar experiments the ester was obtained in 85% yield and in 30% yield,[18] when excess acid was added at −100 and −30°, respectively.

A separate experiment established that (a) when methyl methoxyacetate was added to a reaction mixture formed from the reaction of the *trans* isomer with 0.3 equiv of *n*-butyllithium, it was not destroyed and could be readily detected by gc analysis; (b) when excess 0.5 *N* hydrochloric acid was added to a dilute tetrahydrofuran solution of the *cis* and *trans* isomers, they did not react and no methyl methoxyacetate was formed even after several hours at 25°.

B. Anhydrous Hydrogen Chloride.—The procedure described in A was followed using 0.0167 mol of *trans*-1,2-dimethoxy-1-chloroethylene and 0.015 mol of *n*-butyllithium in 60 ml of tetrahydrofuran–hexane. Gc analysis established that 73% (0.0122 mole) of the *trans* isomer had reacted. At −30° 50 ml of a saturated ether solution of anhydrous hydrogen chloride was added to the reaction mixture, and a yellow-orange color developed then faded rapidly. Gc analysis of an aliquot indicated that 0.0064 mol of *trans*-1,2-dimethoxy-1-chloroethylene and no *cis* isomer had been formed after the addition of hydrogen chloride.

The results from similar experiments are summarized. Ether solutions of anhydrous hydrogen chloride were added at the temperatures indicated: (a) −30°, 0.019 mol of *trans* reacted, 0.0095 mol of *trans* formed; (b) 0 to 10°, 0.0155 mol of *trans* reacted, 0.0020 mol of *trans* formed; (c) 25°, 0.0133 mol of *trans* reacted, 0.000 mol of *trans* formed.

The product *trans*-1,2-dimethoxy-1-chloroethylene was identified from its retention time and from the nmr spectrum of the crude product mixture after evaporation of the solvent. No significant amount of *cis* isomer was formed in any of these experiments. A control experiment established that neither isomer reacted with anhydrous hydrogen chloride in dilute tetrahydrofuran.

C. Miscellaneous Traps.—The general procedure was to treat *trans*-1,2-dimethoxy-1-chloroethylene with slightly less than 1 equiv of *n*-butyllithium in tetrahydrofuran at −100°. Excess trapping reagent was added to the mixture which was held at −70° for several hours and then warmed to 25°. The trapping reagents diphenylisobenzofuran, tetraphenylcyclopentadienone, and 3,4-dicyanofuran were recovered in high yield. When excess cyclopentadiene was used, 45% of the *trans* olefin starting material was recovered, although gc analysis of an aliquot withdrawn prior to addition of cyclopentadiene indicated that 85% of the *trans* isomer had reacted. Examination of the crude reaction mixture (gc, nmr analysis) revealed no evidence of 1:1 or 2:1 adducts of cyclopentadiene and dimethoxyacetylene.

When tetracyanoethylene or dimethylacetylene dicarboxylate was added to the reaction mixture, dark red-violet solutions resulted, and thin layer chromatography of the crude products indicated complex mixtures of highly colored, polar molecules had been formed.

Attempts to Trap Lithium Compound 5a. A.—To a solution of 5.0 g (0.016 mol, 60% *cis*, 40% *trans* isomer) of 1,2-dimethoxy-1-chloroethylene in 50 ml of anhydrous tetrahydrofuran at −100° was added over 30 min 11 ml (*ca.* 0.017 mol) of a 1.6 *M* solution of *n*-butyllithium in hexane. Ten minutes later excess Dry Ice was added and the reaction mixture was warmed to 25°. Gc analysis indicated 80% of the *trans* and 0% of the *cis* isomer had reacted.

A white solid product was collected and dissolved in water (basic). The solution was acidified to pH 4–5 and extracted with methylene chloride to yield 0.27 g of a pale yellow oil: nmr (CCl_4), τ 0.3 (s, 1), 5.57 (s, 2), 5.92 (s, 3), 6.22 (s, 3), 7.7 (m, 2), 8.1–9.3 (m, 7). Further acidification (pH 2) and extraction yielded 0.10 g of valeric acid identified by comparison of the nmr spectrum with that of an authentic sample.

The tetrahydrofuran–hexane solution solution was extracted with water. Acidification of the extract to pH 5 followed by extraction with methylene chloride yielded 0.14 g of a yellow oil; nmr (CCl_4) signals were at τ 0.7 (s, 1), 5.4–6.8 (very complex set of singlets, 9), and 7.5–9.3 (complex multiplets, 11 H). Further acidification (pH 1) and extraction yielded 0.10 g of an oily solid. The nmr spectrum ($CDCl_3$) had several singlets in the methoxyl proton region and an acid proton with a methoxyl to carboxyl proton ratio of 12:1.

---

[18] Yields based on gc analyses were calculated by comparing peak areas with peak areas of solutions of authentic components in concentrations approximating those of the unknown solutions using toluene and/or *cis* olefin as the internal standard in both.

B.—Several other attempts to trap an anionic intermediate from the reaction of the *trans* olefin with 0.8–1.0 equiv of *n*-butyllithium at −100° using Dry Ice were not successful. The only acidic product isolated was valeric acid in small amounts.

Attempts to Trap Lithium Compound 5b. A. 2,3-Dimethoxy-3-chloroacrylic Acid.—To a solution of 3.3 g (0.027 mol) of *cis*-1,2-dimethoxy-1-chloroethylene in 60 ml of anhydrous tetrahydrofuran at −110° was added over 30 min 20 ml (0.030 mol) of *sec*-butyllithium in hexane. The reaction mixture became yellow and solids were present. Gc analysis indicated all the *cis* olefin had reacted. After 100 min at −100° excess Dry Ice was added (yellow color disappeared), and the reaction mixture was warmed to 25°. Distilled water (75 ml) was added, the aqueous extract (pH 7) was acidified to pH 3 with 2 *N* hydrochloric acid, and extracted with several portions of methylene chloride. This extract yielded 1.8 g of a pale yellow solid, mp 87–95°. The aqueous layer was acidified further (pH 1) and a second methylene chloride extraction yielded 1.6 g of a white solid, mp 103–107°. The combined crude product was crystallized from 75:25 hexane–benzene and yielded 2.2 g (*ca.* 45%) of 2,3-dimethoxy-3-chloroacrylic acid, mp 103.5–106.5°. An analytical sample, mp 104.8–105.8° (gas evolved), was obtained by sublimation at 80° (0.05 mm); ir (KBr) bands were at 3600–2400 (broad), 1700 (m), and 1580 cm^{-1} (s); nmr (CDCl$_3$) signals were at τ 0.2 (s, 1), 6.02 (s, 3), and 6.26 (s, 3).

Anal. Calcd for $C_5H_7ClO_4$: C, 36.05; H, 4.24; Cl, 21.28. Found: C, 36.25; H, 4.34; Cl, 21.22.

When the Dry Ice was added to a reaction mixture immediately after the *sec*-butyllithium had been added, about the same yield of acid was obtained.

B. Dilute Acid.—To a solution of 2.4 g (0.019 mol) of *cis*-1,2-dimethoxy-1-chloroethylene and 0.4 ml of toluene in 50 ml of anhydrous tetrahydrofuran at −100° was added over 5 min 15 ml (*ca.* 0.024 mol) of a 1.5 *M* solution of *sec*-butyllithium in hexane. Gc analysis of an aliquot removed after 30 min at −100° indicated 80% of the *cis* isomer had reacted. Dilute hydrochloric acid (10 ml of 0.5 *N*) was added, and the yellow color which had formed upon addition of the *sec*-butyllithium faded rapidly. The reaction mixture was warmed to 25°, and gc analysis showed a threefold increase in the amount of *cis* isomer present over that measured before the acid was added. None of the *trans* isomer was formed, and there was no methyl methoxyacetate.

C. Anhydrous Hydrogen Chloride.—To a reaction mixture of 0.037 mol of *cis*-1,2-dimethoxy-1-chloroethylene and 0.04 mol of *sec*-butyllithium in 125 ml of tetrahydrofuran–hexane which had been at −100° for 4 hr was added 50 ml of a cold (−80°) saturated solution of hydrogen chloride in ether. The solids present dissolved rapidly and gc analysis of an aliquot removed after a few minutes showed 100% recovery of the *cis* isomer.

When the hydrogen chloride solution was added to a reaction mixture which had been at −100° for 2 hr and at −80° for two hr, about 75% of the *cis* isomer was recovered and none of the *trans* isomer was detected. When the addition was made to a reaction mixture which had been at −80° for 5 hr (solids completely dissolved, bright yellow solution), none of the *cis* isomer was recovered, but about 5% of a component with the retention time of the *trans* isomer was detected.

Bis(2-chloro-1,2-dimethoxyvinyl)mercury.—To a dilute solution of 2-chloro-1,2-dimethoxyvinyllithium prepared from 0.05 mol of *cis*-1,2-dimethoxy-1-chloroethylene and 0.05 mol of *sec*-butyllithium in 135 ml of tetrahydrofuran–hexane at −100° was added dropwise 6.0 g (0.02 mol) of mercuric chloride in 20 ml of tetrahydrofuran. The slurry of gray solids which formed was stirred at −75° for 3 hr and then warmed to −60°. At −60°, 20 ml of water was added and the mixture was warmed to 25°. The organic layer was separated, dried over magnesium sulfate, and concentrated to dryness under nitrogen leaving 6.0 g of a fluffy white solid, mp 83–101°. Pure bis(2-chloro-1,2-dimethoxyvinyl)mercury was obtained after two crystallizations from 3:1 hexane–benzene as white needles: mp 114–116°; ir (CHCl$_3$), 2920 (s), 2810 (m), 1605 (s), 1438 (s), 1080–1140 (vs), 1025 (s), 939 (s), 820 (s) cm^{-1}; nmr (CDCl$_3$), τ 6.29 (s, 3), 6.21 (s, 3).

Anal. Calcd for $C_8H_{12}O_4Cl_2Hg$: C, 21.65; H, 2.73; Cl, 15.98; Hg, 45.21. Found: C, 21.70; H, 2.76; Cl, 16.25; Hg, 45.42.

Thermolysis of Bis(2-chloro-1,2-dimethoxyvinyl)mercury.—Bis(2-chloro-1,2-dimethoxyvinyl)mercury (1.0 g) was heated under nitrogen in a short path still at 180–200° for 4 hr. The mercurial melted, the melt became dark red and gradually deposited a gray-black solid. Little or no volatile material distilled from the melt. The crude mixture was extracted with methylene chloride and about 0.4 g of mercury metal was recovered. The methylene chloride-soluble fraction was a mixture of at least six components according to thin layer chromatography.

Silver 3-Chloro-2,3-dimethoxyacrylate.—3-Chloro-2,3-dimethoxyacrylic acid (1.4 g, 0.0084 mol) was dissolved in 30 ml of distilled water and enough concentrated ammonium hydroxide was added to dissolve the acid and bring the pH to 8. Silver nitrate (1.7 g, 0.01 mol) was added and the impure product was collected as 1.4 g of a white crystalline solid, mp 150–153° dec.

Anal. Calcd for $C_5H_6ClO_4Ag$: C, 21.96; H, 2.20; Cl, 12.97. Found: C, 23.66, 23.78; H, 2.62, 2.53; Cl, 13.37.

Thermolysis of Silver 3-Chloro-2,3-dimethoxyacrylate.—The crude silver salt (1.4 g) was dissolved in 75 ml of anhydrous acetonitrile and refluxed for 4 hr under nitrogen. No gas was evolved, and a shiny silver mirror was deposited on the walls of the flask. The acetonitrile-insoluble product was collected as 0.5 g of a gray powder which was insoluble in ammonium hydroxide.

Anal. Found: Ag, 82.84, 82.70.

Registry No.—**2a,** 16012-08-1; **2b,** 16012-09-2; *n*-butyllithium, 109-72-8; *sec*-butyllithium, 598-30-1; **3,** 16012-10-5; bis(2-chloro-1,2-dimethoxyvinyl)mercury, 16012-11-6; silver 3-chloro-2,3-dimethoxyacrylate, 16048-06-9.