of 56.4 Mc./sec. with trifluoroacetic acid as an internal reference. Triphenylphosphinemethyliminetrifluoroboron (**1**) showed a single peak at a lower field (3660 c.p.s.), thus confirming the equivalence of the fluorine atoms in the complex. The fluorine chemical shift in methylaminotriphenylphosphonium tetrafluoroborate (**5**) was found to be at 4170 c.p.s.

Experimental[11]

Triphenylphosphinealkyliminetrifluoroboron Complexes.—An appropriate triphenylphosphinalkylimine (0.01 mole) was dissolved in 300 ml. of ether, which had been dried over sodium. The solution was cooled to −72° and boron trifluoride gas (after drying over phosphorus pentoxide) was passed through it at a rate of 2–3 bubbles/sec. The respective triphenylphosphinealkyliminetrifluoroboron complex started to precipitate as a white precipitate. After completion of the reaction the passage of BF_3 was stopped and the reaction mixture was stirred for a few minutes. The precipitate was then collected by suction filtration and dried under vacuum over phosphorus pentoxide. Throughout these operations a dry nitrogen atmosphere was maintained. Analytical samples were prepared by dissolving the compounds in acetone, filtering, and reprecipitating them by adding ether to the filtrate.

Alkylaminotriphenylphosphonium Tetrafluoroborate.—When the above reaction was carried out under ordinary room conditions instead of a dry nitrogen atmosphere, the products isolated were exclusively alkylaminotriphenylphosphonium tetrafluoroborates. They were obtained analytically pure by recrystallization from a chloroform–ethyl acetate mixture.

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[11] Melting points are uncorrected. Microanalysis was by A. Bernhardt, Mulheim/Ruhr, Germany, and by Galbraith Laboratories, Knoxville, Tenn.

The Reaction of Silver 2-Bromo-3-methyl-2-butenoate with 1,1-Diphenylethylene

H. D. Hartzler

Contribution No. 982 from the Central Research Department, Experimental Station, E. I. duPont de Nemours and Company, Wilmington, Delaware

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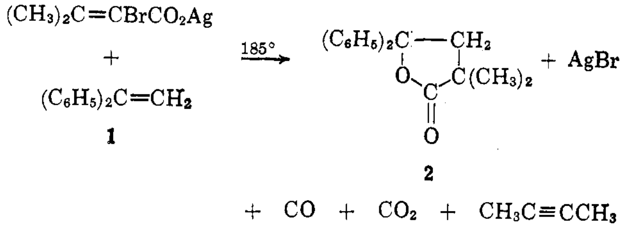
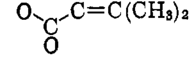
In the course of examining reactions intended to generate methylene carbenes[1] we briefly investigated the thermal decomposition of some silver salts of α-bromo-α,β-unsaturated acids. Analogous salt decompositions have been useful in the generation of benzyne,[2] carbon dichloride,[3] and carbon difluoride.[4]

The silver salts of 2-bromo-3-methyl-2-butenoic acid, 2-bromo-3,3-diphenylacrylic acid, and 2-bromo-3-biphenyleneacrylic acid were prepared. All decomposed in the range 185–205° with gas evolution and formation of silver bromide. Thermal decomposition of these salts suspended in olefins gave complex mixtures. Hydrocarbons were minor reaction products and methylenecyclopropanes were not found.

The decomposition of silver 2-bromo-3-methyl-2-butenoate (**1**) in 1,1-diphenylethylene gave a peculiar result. 2,2-Dimethyl-4,4-diphenyl-γ-butyrolactone (**2**) was formed consistently in yields of 20–25%. Silver bromide was formed in 98% yield. The gaseous products were carbon monoxide (35%), carbon dioxide (12%), and traces of 2-butyne. Repeated attempts to prove that the lactone was the unsaturated lactone **3** failed; so recourse was made to proving structure **2**.





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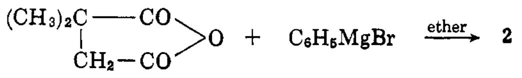
The n.m.r. spectrum of **2** showed the resonances of the methyl groups (singlet) at τ 8.90, the methylene (singlet) at 7.08, and the phenyl at 2.6. The intensities were the expected 3:1:5. The benzhydrilic lactone was readily hydrogenolyzed with palladium catalyst to give 2,2-dimethyl-4,4-diphenylbutyric acid in 95% yield. The n.m.r. spectrum of this acid showed the resonances of the methyl groups (singlet) at τ 8.83, the methylene (doublet) centered at 7.50, the methine (triplet) centered at 5.83, the aromatic hydrogens at 2.6, and the carboxylic acid hydrogen at −1.76. The intensity ratios were 6:2:1:10:1, respectively.

The lactone **2** was synthesized independently by the addition of phenylmagnesium bromide to unsymmetrical dimethylsuccinic anhydride. There is ample precedent for this type of reaction of anhydrides.[5] In this case, addition proceeds cleanly at the sterically unhindered carbonyl. No isomeric 3,3-dimethyl-4,4-diphenyl-γ-butyrolactone was found in the reaction product. This synthesis gave lactone **2** in 23% yield which was identical in all respects with that obtained from the salt decomposition. The mechanism of the formation of **2** was not investigated.



Experimental[6]

Silver 2-Bromo-3-methyl-2-butenoate.—2-Bromo-3-methyl-2-butenoic acid[7] (26 g., 0.15 mole) was stirred in 200 ml. of water and was dissolved by the addition of ammonium hydroxide. The silver salt was precipitated by the addition of a solution of 25.5 g. of silver nitrate in 25 ml. of water. The solid was filtered and

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[1] H. D. Hartzler, *J. Am. Chem. Soc.*, **86**, 526 (1964).

[2] H. E. Simmons, *J. Org. Chem.*, **25**, 691 (1960).

[3] W. M. Wagner, *Proc. Chem. Soc.*, 229 (1959).

[4] J. M. Birchall, G. W. Cross, and R. N. Haszeldine, *ibid.*, 81 (1960).

[5] M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall Co., Inc., New York, N. Y., 1954, pp. 846-869.

[6] Melting points are uncorrected. N.m.r. spectra were obtained in deuteriochloroform solutions on a Varian A-60 spectrometer. Infrared spectra were obtained on a Perkin-Elmer Model 21 spectrometer.

[7] L. N. Owen and M. V. S. Sultanbawa, *J. Chem. Soc.*, 3089 (1949).

washed with water (two 100-ml. portions), ethanol (three 100-ml. portions), and ether (three 100-ml. portions). After suction drying, the silver salt (29.06 g.) melted at 180–183° dec., with gas evolution and with solid residue.

Anal. Calcd. for $C_5H_6AgBrO_2$: C, 21.00; H, 2.12; Ag, 37.73; Br, 27.95. Found: C, 20.65; H, 2.26; Ag, 37.95; Br, 27.40.

The salt in ethanol had absorption in the ultraviolet at 247 mμ with ϵ >1100. An accurate extinction coefficient was not obtained because of limited solubility.

Reaction of Silver 2-Bromo-3-methyl-2-butenoate with 1,1-Diphenylethylene.—A mixture of 5.72 g. (0.02 mole) of the silver salt and 18 g. (0.10 mole) of diphenylethylene was stirred under nitrogen and heated at 185° for 2 hr. Only 205 ml. of gas (STP, 0.0094 mole, 47%) was evolved. Mass spectroscopic analysis of the gas showed it to be mainly CO and CO_2 in a ratio of 3:1. Traces of dimethylacetylene were found (<0.5%). The mixture was cooled and filtered. The solid was rinsed with benzene, leaving 3.68 g. (98% of theoretical silver bromide) of insoluble salt. The filtrate was distilled to recover 13.7 g. of diphenylethylene. The distillation residue was chromatographed on Florisil to give a crude hydrocarbon (0.10 g., m.p. 48–60°) and a lactone (0.56 g.) which melted at 116.6–117° after recrystallization from hexane. The lactone was identified as 2,2-dimethyl-4,4-diphenyl-γ-butyrolactone (**2**).

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.17, 81.23; H, 6.67, 6.74.

The infrared spectrum of **2** showed absorption at 5.64 μ, consistent with the γ-lactone formulation. The ultraviolet spectrum of **2** in ethanol showed only the absorption of a monosubstituted aromatic system.

Hydrogenolysis of 2,2-Dimethyl-4,4-diphenyl-γ-butyrolactone.—The lactone (0.5092 g., 1.832 mmoles), obtained from the above reaction, was hydrogenated in methanol solution with 10% palladium on carbon as catalyst. After removing catalyst and solvent, there was obtained after recrystallization from hexane 0.48 g. of an acid, m.p. 109.5–111°, which was identified as 2,2-dimethyl-4,4-diphenylbutyric acid.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.5; H, 7.51. Found: C, 81.27, 81.42; H, 7.51, 7.56.

The infrared spectrum of the acid had broad absorption in the 3 to 4-μ region and absorption at 5.89 μ, indicating the carboxylic acid function. The ultraviolet spectrum of the acid in methanol was that of a substituted benzene.

Synthesis of 2,2-Dimethyl-4,4-diphenyl-γ-butyrolactone.—A solution of 5.23 g. (0.041 mole) of unsymmetrical dimethylsuccinic anhydride in 55 ml. of tetrahydrofuran was cooled to −80°. A solution of phenylmagnesium bromide in ether (29 ml. of 3 *M* solution, 0.087 mole) was dropped into the anhydride solution over a period of 1 hr. at −60 to −80°. The mixture was decomposed with dilute aqueous hydrochloric acid, and the ether-soluble product was separated. Evaporation of the ether left a residue from which 2.56 g. (23.6%) of the crude lactone (m.p. 108–114°) was separated by trituration with hot benzene. Upon recrystallization from hexane, the lactone melted at 115–116.5°. A mixture melting point with the material obtained above was not depressed. The infrared spectra of the two samples were identical.

Separation and Determination of the Hydrolysis Products of a Methylated Xylan as Their Trimethylsilyl Derivatives by Vapor Phase Chromatography

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Following the encouraging results of Hedgley and Overend[1] on the thermal stability, relative volatility, and vapor phase chromatography of several carbohydrate trimethylsilyl derivatives, the application of these derivatives for xylan structure analysis by vapor phase chromatography was considered. Ferrier[2] compared the gas–liquid chromatographic mobilities of the isomeric tetra-*O*-trimethylsilylpentoses and methyl tri-*O*-trimethylsilylpentopyranosides obtained by the method of Hedgley and Overend[1] and interpreted these in terms of molecular conformations. More recently, Sweeley, *et al.*,[3] reported an improved procedure for the preparation of, as well as vapor phase chromatographic data on, a large number of carbohydrate trimethylsilyl derivatives.[4] The data reported here were obtained on trimethylsilyl derivatives prepared by the procedure of Sweeley, *et al.*, except that instead of heating relatively insoluble carbohydrates in pyridine to dissolve them they were shaken with the reaction mixture at room temperature until dissolution and reaction were complete. D-*manno*-Heptulose required 3 hr., but 10 min. was sufficient in most cases. This procedure was preferred since the trimethylsilyl derivatives, one formed, are relatively stable in the reaction mixture. Chromatograms of such a reaction mixture containing eighteen carbohydrates and excess reagents in pyridine showed no discernible degradation or anomerization when stored at room temperature in a plastic-stoppered vial and analyzed periodically for up to 4 months.

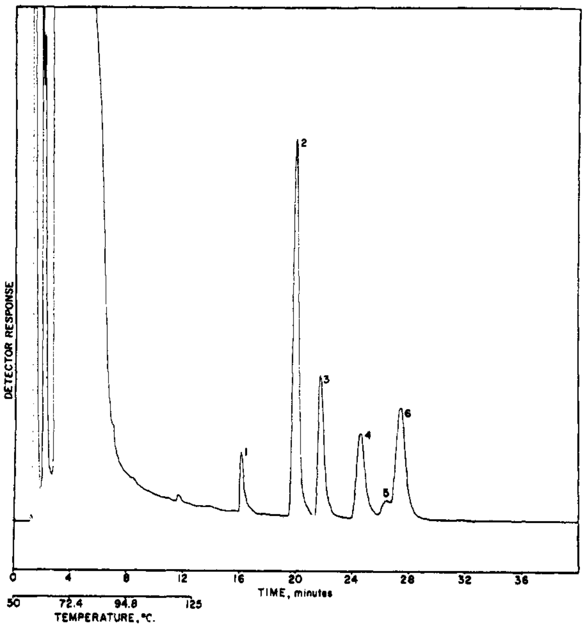

Fig. 1.—Separation of the trimethylsilyl derivatives obtained from crystalline **1**, 2,3,4-tri-*O*-methyl-α-D-xylose; **2**, 2,3-di-*O*-methyl-α-D-xylose; **3**, 4-*O*-methyl-D-xylose; **6**, 2-*O*-methyl-β-D-xylose; and **4** and **5**, a partially crystalline mixture of 3-*O*-methyl-α- and -β-D-xylose. The chromatogram was made with a 6 ft. × 0.25 in. o.d. copper tube packed with 3% SE 52 on Gas-Chrom A, programmed from 50° by 5.6°/min. to 125° at which temperature it was held. The instrument used was a F. and M. Model 500 with flame ionization attachment.

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(1) E. J. Hedgley and W. G. Overend, *Chem. Ind.* (London), 378 (1960).

(2) R. J. Ferrier, *Tetrahedron*, **18**, 1149 (1962).

(3) C. C. Sweeley, R. Bentley, M. Makita, and W. W. Wells, *J. Am. Chem. Soc.*, **85**, 2497 (1963).

(4) Since this paper was submitted, M. B. Perry [*Can. J. Biochem.*, **42**, 451 (1964)] has reported on the separation, determination, and characterization of 2-amino-2-deoxy-D-glucose and 2-amino-2-deoxy-D-galactose by vapor phase chromatography of their trimethylsilyl derivatives. Similarly, W. W. Wells, T. Katagi, R. Bentley, and C. C. Sweeley [*Biochim. Biophys. Acta*, **82**, 408 (1964)] have reported the vapor phase chromatographic separation of sugar phosphate esters as their trimethylsilyl derivatives.