

The Addition of Methylchlorosilane to Butyne-2

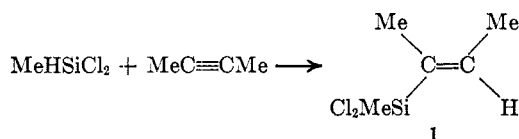
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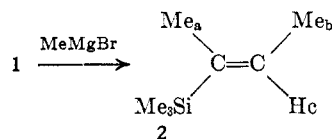
In the presence of chloroplatinic acid or platinum catalysts, silicon hydrides add to both terminal and nonterminal olefins to form primary alkylsilanes.^{1,2} The unusual tendency toward making primary alkylsilanes from nonterminal olefins and for olefins to isomerize during the reaction has been studied by several groups of investigators.³⁻⁶

We wish to report that no such rearrangement occurs with butyne-2. Methylchlorosilane adds to butyne-2 stereospecifically in a *cis* manner at the original position of the triple bond to form *cis*-2-methylchlorosilylbutene-2 (1). That the reaction led to *cis* addition



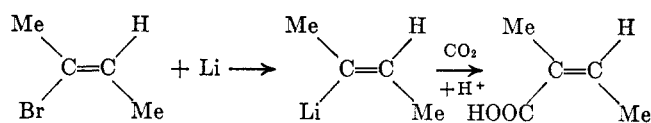
is in agreement with the results of Benkeser⁷ which showed that in the presence of chloroplatinic acid or supported platinum catalysts trichlorosilane added to 1-alkynes in a *cis* manner to form *trans*-1-trichlorosilyl-1-alkenes as the major products.

Treatment of the adduct 1 with methylmagnesium bromide formed *cis*-2-trimethylsilylbutene-2 (2).



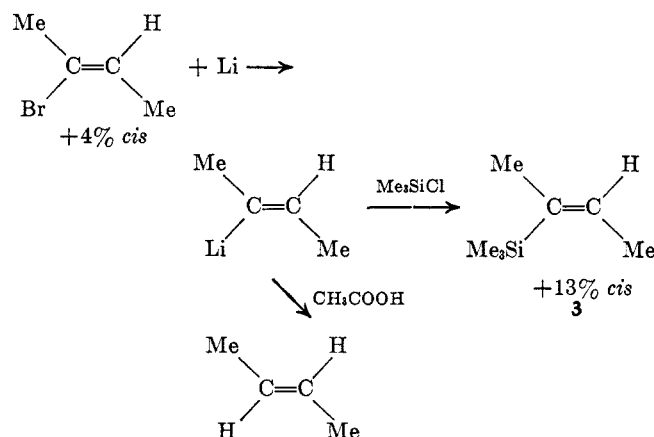
The H¹ nuclear magnetic resonance (nmr) spectrum of 2 was examined in detail using spin-decoupling methods. A relatively large J_{ac} coupling (2.0 cps) would indicate that methyl group a and the vinylic H atom are situated *trans* to each other. In addition the small value observed for J_{ab} in 2 (0.9 cps) indicates that the methyl groups are in a *cis* configuration. These conclusions are based on interpretations of the nmr spectra of *cis*- and *trans*-2-bromobutene-2 published by Richards and Beach.⁸

Further confirmation of our assignment of a *cis* configuration to 2 is based on the synthesis of *trans*-2-trimethylsilylbutene-2 (3). Dreiding and Pratt⁹ prepared angelic acid in 91% isomeric purity by carbonation of the organolithium derivative formed from *trans*-



2-bromobutene-2. The work of these authors plus the references cited in their publication provide convincing evidence that the formation of the vinyl lithium species and its coupling with various reagents can be accomplished with only minor loss of the configuration of the groups about the double bond.

The lithium reagent from *trans*-2-bromobutene-2 reacted with trimethylchlorosilane to form *trans*-2-trimethylsilylbutene-2 (3) which we judged from its infrared spectrum to be contaminated by 13% of 2. The



same lithium reagent with acetic acid produced essentially pure *trans*-butene-2, as judged by its infrared spectrum. Thus we are able to relate the configuration of methyl groups in 3 to those of *trans*-butene-2.

Experimental Section

***cis*-2-Trimethylsilylbutene-2 (2).**—Butyne-2 (27 g, 0.5 mole) and chloroplatinic acid (10^{-5} mole) were placed in a small flask equipped with a reflux condenser. Methylchlorosilane (0.45 mole) was slowly added. The solution was cooled with a water bath to maintain its temperature at 25–30°. The product was added to an excess of methylmagnesium bromide in ether. After the usual work-up and distillation, *cis*-2-trimethylsilylbutene-2 was recovered boiling at 110°: n_D^{25} , 1.4245; d_{25} 0.7461; R_D^{10} 0.3423, R_D calcd 0.3403; yield 27 g (47%).

Anal. Calcd for $C_7H_{16}Si$: C, 65.5; H, 12.55; Si, 21. Found: C, 65.4, 65.4; H, 12.40, 12.53; Si, 21.5.

The infrared spectrum showed characteristic bands at 1620 (C=C stretch), 1375 (MeC), and 1243 (MeSi), as well as three strong unassigned bands at 610, 460, and 403 cm^{-1} which were used to assay this compound in mixtures.

The nmr spectrum showed a singlet absorption at τ 9.98 (MeSi), a complex system of peaks at 8.4 (both methyl groups on carbon), and a complex peak system at 4.3 (vinylic hydrogen). A spin-decoupling experiment¹¹ showed a vinylic hydrogen spectrum composed of a 1:3:3:1 quartet of 1:3:3:1 quartets with coupling constants 6.8 and 2.0 cps. The 6.8 coupling constant is assigned to geminal CH_2CH and the 2.0-cps coupling to a *trans* $\text{CH}_2\text{C}=\text{H}$ system. The five-band CH_2CH_2 coupling displayed by the methyl group absorption (a doublet of quartets) is 0.9 cps which indicates a *cis* arrangement of the methyl groups.⁸

***trans*-2-Bromobutene-2.**—A mixture of *cis*- and *trans*-2-bromobutene-2 (Columbia Organic Chemicals) was carefully fractionated using a small spinning-band column. The various fractions were assayed by gas-liquid partition chromatography (glpc). *trans*-2-Bromobutene-2 was isolated in 99% purity:

(10) R_D is the symbol for the specific refraction of a transparent substance at the D wavelength of sodium light.

(11) We thank Dr. E. B. Baker of The Dow Chemical Co. who carried out the spin-decoupling experiment described here.

(1) J. L. Speier, J. A. Webster, and G. H. Barnes, *J. Am. Chem. Soc.*, **79**, 974 (1957).

(2) J. C. Saam and J. L. Speier, *ibid.*, **80**, 4104 (1958).

(3) J. C. Saam and J. L. Speier, *ibid.*, **83**, 1351 (1961).

(4) J. W. Ryan and J. L. Speier, *ibid.*, **86**, 895 (1964).

(5) T. G. Selin and R. West, *ibid.*, **84**, 1863 (1962).

(6) R. A. Benkeser, Paper M-7, International Symposium on Organosilicon Chemistry, Prague, Czechoslovakia, 1965.

(7) R. A. Benkeser and R. A. Hickner, *J. Am. Chem. Soc.*, **80**, 5298 (1958).

(8) J. H. Richards and W. F. Beach, *J. Org. Chem.*, **26**, 623 (1961).

(9) A. S. Dreiding and R. J. Pratt, *J. Am. Chem. Soc.* **76**, 1902 (1954).

n_D^{25} 1.4566; d_{25}^{25} 1.318; R_D 0.2065, R_D calcd 0.2065. Dreiding and Pratt report n_D^{25} 1.4561 for this compound.⁹

trans-2-Trimethylsilylbutene-2 (3).—*trans*-2-Bromobutene-2 (6.7 g, 0.05 mole) was slowly added to a flask containing lithium wire (0.70 g, 0.10 g-atom) and ether at a temperature of 0°. When the organolithium reagent had been formed, trimethylchlorosilane (5.4 g, 0.05 mole) was added. The resulting solution was filtered, washed, and dried. A sample of **3** was then isolated by distillation and judged to be 96% pure by glpc, n_D^{25} 1.4252.

The infrared spectrum of this material showed the same group bands at 1620, 1375, and 1243 cm^{-1} as **2**. The bands at 610, 460, and 403 cm^{-1} were present at much lower intensity in this sample from which we estimate that this material contains 13% of **2**.

This sample exhibited strong absorptions at 643, 485, and 432 cm^{-1} which we believe to be characteristic of the *trans* isomer **3**.

trans-Butene-2.—*trans*-2-Bromobutene-2 (6.7 g, 0.05 mole) was slowly added to lithium wire (0.70 g, 0.10 g-atom) in ether at 0° with stirring. When the organolithium reagent had formed the solution was treated with acetic acid (3 ml) and the butene which was evolved was collected in a cold trap and distilled to a second cold trap to free it of ether. The infrared spectrum of this material was that reported for *trans*-butene-2¹² except for the presence of about 4% ether.

(12) American Petroleum Institute, Research Project 44, Infrared Spectral Data, Spectra No. 908, 909.

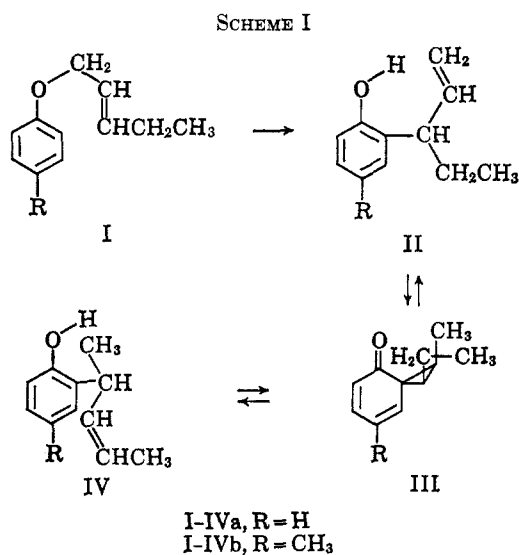
On the Reversibility of the "Abnormal Claisen Rearrangement"^{1a}

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The "abnormal" product IVa (Scheme I) of the Claisen rearrangement of γ -ethylallyl phenyl ether (Ia) has been shown to be formed from the normal product

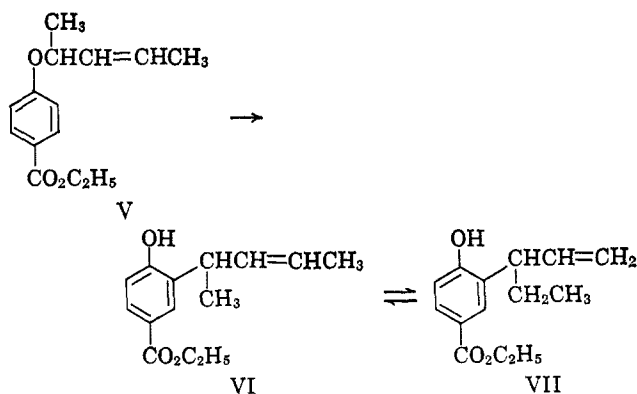


IIa by a secondary thermal rearrangement.² Both normal and "abnormal" products have usually been detected in the cases examined,³ but it was reported that

(1) (a) Financial support by the Robert A. Welch Foundation and the University of Texas Research Institute is gratefully acknowledged; (b) University of Texas Predoctoral Fellow, 1964-1965.

(2) (a) E. N. Marvell, D. R. Anderson, and J. Ong, *J. Org. Chem.*, **27**, 1109 (1962); (b) A. Habich, R. Barner, W. von Philipsborn, and H. Schmid, *Helv. Chim. Acta*, **48**, 1297 (1965).

when IIa was heated for a long time at 200-230°, the conversion to IVa was complete,⁴ as well as could be detected by the infrared analysis used. According to the accepted mechanism,^{2,5} the rearrangement of IIa to IVa *via* the spirodienone intermediate IIIa should be reversible. Although IVa would be expected to be favored in an equilibrium between IIa and IVa, there is one report in the literature which suggests that IIa should be present in a detectable amount. When the ether V was subjected to thermal rearrangement, a mixture of products was obtained which was shown by ozonolysis to contain some VII.^{3a}



We decided to test the reversibility of the rearrangement in this α -ethylallyl II, VII and α,γ -dimethylallyl IV, VI system using the *p*-cresol derivatives IIb and IVb, which were available to us.

Thermolysis of γ -ethylallyl *p*-tolyl ether (Ib) at temperatures of 175-200° gave mixtures of IIb and IVb; higher temperatures and longer heating times gave increased amounts of IVb, as expected, but vpc, nmr, and infrared data revealed evidence of the presence of both isomers in all reaction products.

Authentic samples of IIb and IVb were prepared by independent syntheses.^{6,7} Preliminary experiments in which IVb was heated at 185-200° gave product mixtures that were difficultly resolved by vpc, but definitely contained small amounts of IIb. Better separation of IIb from IVb was accomplished by converting the mixed isomeric phenols to their methyl ethers before applying preparative-scale vapor phase chromatography. In this way, a sample of the methyl ether of IIb was obtained which was pure enough for positive identification by vpc, nmr, and infrared analysis.

In order to demonstrate formation of the same equilibrium mixture of IIb and IVb from either isomer by thermal rearrangement, separate samples of IIb and IVb were heated in *N,N*-diethylaniline at 200° for 9 days. Analysis of the phenolic components of the two reaction mixtures showed them to be identical and to consist of ca. 96% IVb and ca. 4% IIb.

These results support the view that the secondary rearrangement of an α -ethylallylphenol (II) to an α,γ -dimethylallylphenol (IV), which is responsible for "ab-

(3) (a) W. M. Lauer and H. E. Ungnade, *J. Am. Chem. Soc.*, **61**, 3047 (1939); (b) other references given there.

(4) D. R. Anderson, Ph.D. Thesis, Oregon State University, 1962, pp 23, 43 (through University Microfilms, Inc., Ann Arbor, Mich.).

(5) (a) R. M. Roberts and R. G. Landolt, *J. Am. Chem. Soc.*, **87**, 2281 (1965); (b) R. M. Roberts, R. N. Greene, R. G. Landolt, and E. W. Heyer, *ibid.*, **87**, 2282 (1965).

(6) A. Habich, R. Barner, R. M. Roberts, and H. Schmid, *Helv. Chim. Acta*, **45**, 1943 (1962).

(7) N. Kornblum and A. P. Lurie, *J. Am. Chem. Soc.*, **81**, 2705 (1959).