The Synthesis of Tetravinylmethane

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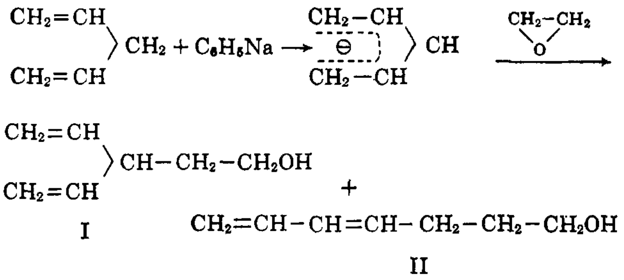
Although the tetravinyl derivatives of the Group IV elements silicon,[1a] germanium,[1b] tin,[1c] and lead[1d] have been reported, the corresponding tetravinylmethane has until now remained unknown. We now wish to report the synthesis of this compound by a novel reaction sequence.

1,4-Pentadiene was treated with a heptane suspension of phenylsodium, and the resulting mixture was treated with ethylene oxide, affording on work-up 3-vinyl-4-penten-1-ol (I) and 4,6-heptadien-1-ol (II).



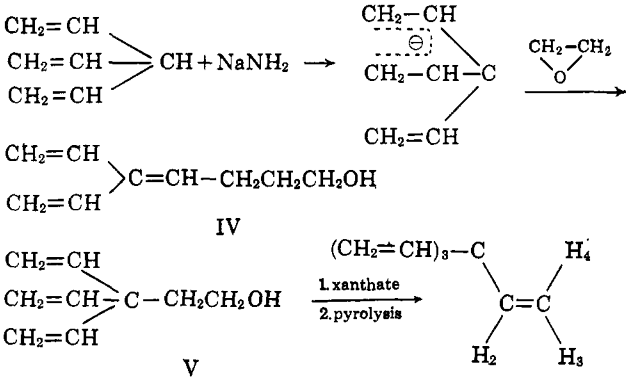
The mixture of I and II, obtained in 50–60% yield, was found to consist of 60–70% I. The isomeric alcohols were readily separated by fractional distillation: I, b.p. 53–55° (6 mm); II, b.p. 65–67° (6 mm). The structure of compound I was established by its infrared spectrum which showed bands at 1640 cm.$^{-1}$ (nonconjugated C=C stretch) and characteristic vinyl C–H bands at 3090, 3010, 1850, 1420, 992, and 913 cm.$^{-1}$.[2] Compound II exhibits a double band at 1640 and 1595 cm.$^{-1}$ (conjugated C=C), and bands at 1000, 945, and 898 cm.$^{-1}$ (C–H out-of-plane deformation assigned to *trans* internal conjugated olefin).

The n.m.r. spectrum of I showed absorption for two methylene hydrogens at 8.38, one tertiary allylic hydrogen at 7.14, two methylol hydrogens at 6.43, one hydroxyl hydrogen at 5.98, four terminal methylene hydrogens (multiplet) at 4.97, and two internal vinyl hydrogens at 4.24 τ. In addition, the spin–spin splittings and coupling constants are all consistent with structure I.

Compound II showed absorption for two hydrogens ($-CH_2-CH_2OH$) at 8.34, two allylic hydrogens at 7.86, two methylol hydrogens at 6.46, one hydroxyl hydrogen at 5.84, and five hydrogens comprising the conjugated system as a complex multiplet between 5.28 and 3.52 τ.

Compound I was converted to the xanthate, which was pyrolyzed at 250–300° to give 3-vinyl-1,4-pentadiene (trivinylmethane)[3] in 20–40% yield.

Trivinylmethane was treated with sodamide in liquid ammonia to give an intensely colored red solution. Reaction with ethylene oxide gave 5-vinyl-4,6-heptadien-1-ol (IV, 23%) and 3,3-divinyl-4-penten-1-ol (V, 77%) in 80% yield.



Compounds IV and V were again easily separable by fractional distillation.

The infrared spectrum of V showed virtually the same absorptions already mentioned in connection with I, characteristic of terminal nonconjugated unsaturation, while IV exhibited a spectrum strongly indicative of conjugation (see Experimental).

Conversion of V to the xanthate and subsequent pyrolysis gave 3,3-divinyl-1,4-pentadiene (tetravinylmethane). The hydrocarbon showed bands in the infrared typical of terminal unsaturation (see Experimental), and a similarly typical[4] ABC grouping in its n.m.r. spectrum: $\tau_2 = 4.18$, $\tau_3 = 4.91$, $\tau_4 = 4.99$; $J_{23} = 8.75$, $J_{24} = 18.5$, $J_{34} = 2.0$ c.p.s. The area ratio of $H_3 + H_4$ to H_2 was 2.08 to 1.00 and no other absorptions were present.

Although the sodium derivatives of both 1,4-pentadiene and trivinylmethane have been reported[3,5] to give products arising almost exclusively from attack of the carbanion at the primary position, results obtained in these laboratories have indicated a more complex nature to the reactions of these species. The results of this investigation will be the subject of a future publication.

Experimental[6]

Reaction of Sodium Pentadiene with Ethylene Oxide.—1,4-Pentadiene (70 g., 1.03 moles) was added to a well-stirred suspension of phenylsodium (1.0 mole) in *n*-heptane. A slight rise in temperature was noted and the originally black suspension turned green. After stirring for 4.5 hr., ethylene oxide (45 g., 1.02 moles) in an equal volume of heptane was added maintaining the temperature below 35°. The resulting mixture was carefully decomposed with water; the organic layer was separated, washed, dried, and the solvent was distilled. The residue was distilled through a 24-in. tantalum spiral column to separate the olefinic alcohols from a considerable amount of β-phenylethanol, and the distillate was refractionated through an 18-in. spinning band column to give 3-vinyl-4-penten-1-ol (30.9 g.), b.p. 53–55° (6 mm), $n^{22}\text{D}$ 1.4530.

Anal. Calcd. for $C_7H_{12}O$: C, 75.00; H, 10.71. Found: C, 75.32; H, 10.81.

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[1] (a) S. D. Rosenburg, J. J. Walburn, T. D. Stankovich, A. E. Balint, and H. E. Ramsden, *J. Org. Chem.*, **22**, 1200 (1957); (b) D. Seyferth, *J. Am. Chem. Soc.*, **79**, 2738 (1957); (c) S. D. Rosenburg, A. J. Gibbons, and H. E. Ramsden, *ibid.*, **79**, 2137 (1957); D. Seyferth and F. G. A. Stone, *ibid.*, **79**, 515 (1957); (d) E. C. Juenge and S. E. Cook, *ibid.*, **81**, 3578 (1959); B. Bartocha and M. Y. Gray, *Z. Naturforsch.*, **14b**, 350 (1959); L. Maier, *Angew. Chem.*, **71**, 161 (1959).

[2] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, Chapter III.

[3] R. Paul and S. Tchelitcheff, *Compt. rend.*, **232**, 1939 (1951).

[4] "High Resolution NMR Spectra," Varian Associates, Palo Alto, Calif., 1962; J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp. 238–246.

[5] R. Paul and S. Tchelitcheff, *Compt. rend.*, **224**, 1118 (1947); *idem.*, *Bull. soc. chim. France*, 108 (1948).

[6] All boiling points are uncorrected. Infrared spectra were determined with a Beckman Model IR-8 spectrophotometer. N.m.r. spectra were determined on a Varian A-60, 60-Mc./sec. high resolution spectrometer

In addition, 4,6-heptadien-1-ol (20.6 g.), b.p. 65–67° (6 mm), n^{22}_D 1.4882, was obtained. This material polymerized to a colorless viscous oil upon standing for several days.

Anal. Found: C, 74.93; H, 11.30.

Trivinylmethane.—3-Vinyl-4-penten-1-ol (100 g., 0.89 mole) was added slowly to an ether suspension of sodium hydride (23.5 g., 0.98 mole), and the mixture then was heated at reflux for 4 hr. Upon cooling, carbon disulfide (67.3 g., 0.89 mole) was added cautiously, and the resulting mixture again was heated at reflux for 1.5 hr. At the end of this time, methyl iodide (124 g., 0.88 mole) was added, and the mixture was heated for a final 1.5 hr. Solids were then dissolved by adding water, and the ether solution was separated, dried, and the ether was removed to give the crude xanthate (195 g.) which was pyrolyzed at 250–300° without further purification. The volatile pyrolysate was washed twice with 40% sodium hydroxide, then with water, and finally with saturated mercuric chloride solution. Distillation through an 18-in. spinning band column gave trivinylmethane (15 g.), b.p. 76.9°, n^{24}_D 1.4238 (lit.[3] b.p. 77°, n^{20}_D 1.4384).

Infrared spectrum (neat, liquid) showed bands at 3090(s), 3010(m), 2975(m), 1830(w), 1630(m), 1410(m), 992(s), 916(s), 691(m) cm.$^{-1}$.

The n.m.r. spectrum of this product showed absorptions at $\tau = 6.33$ (quartet) assigned to the tertiary proton, and typical ABC type olefinic absorption: $\tau_2 = 4.20$, $\tau_3 = 4.97$, $\tau_4 = 5.01$; $J_{23(\mathrm{cis})} = 9.0$, $J_{24(\mathrm{trans})} = 17.5$, $J_{34} = 2.5$ c.p.s. The H_2 quartet was split by the tertiary hydrogen into an octet with $J = 6.0$ c.p.s.

Reaction of Sodium Trivinylmethane with Ethylene Oxide.—Trivinylmethane (19.2 g., 0.20 mole) was added slowly to a suspension of sodamide in 75 ml. of liquid ammonia, prepared from 5.1 g. (0.22 g.-atom) of sodium. Ethylene oxide (10 g., 0.23 mole) was then added cautiously to the resulting deeply colored solution, and the ammonia was then replaced as solvent by ether. After the ammonia had been displaced, another 1 g. of ethylene oxide was added, and the reaction mixture was decomposed slowly with water. The ether layer was separated, washed, and dried. Removal of solvent gave 23.5 g. of light yellow crude alcohols. Gas chromatography showed the mixture to consist of 77% V and 23% IV. Distillation gave V, b.p. 48–50° (0.5 mm), n^{24}_D 1.4769, and IV, b.p. 57–60° (0.5 mm), n^{24}_D 1.5090.

Compound V showed significant bands in the infrared at 3330 (s, broad), 3090(s), 3005(m), 2970(m), 2940(s), 2895(sh), 1840 (w), 1630(m), 1405(m), 1045(s), 1023(s), 1000(s), 918(s) cm.$^{-1}$ (neat, liquid).

Anal. Calcd. for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.16; H, 9.74.

Compound IV showed bands in the infrared at 3330(s), 2090 (m), 3010(m), 2955(s), 2870(m), 1800(w), 1620(m), 1595(m), 1420(m), 1052(s, broad), 978(s), 908(s), 850(m) cm.$^{-1}$ (neat, liquid). Upon standing for several days, IV was transformed into a clear, colorless polymer.

Tetravinylmethane.—The xanthate of 3,3-divinyl-4-penten-1-ol was prepared, in the same manner as previously described for 3-vinyl-4-penten-1-ol, from 14.1 g. of the alcohol, 2.4 g. of sodium hydride, 8.4 g. of carbon disulfide, and 15.5 g. of methyl iodide. The yield of crude xanthate was 21.5 g.

Pyrolysis yielded a light yellow liquid which was washed twice with concentrated potassium hydroxide solution, once with water, and finally with saturated mercuric chloride solution. The organic material was then dried and distilled through an 18-in. spinning band column to give 4.8 g. of tetravinylmethane, b.p. 119.5–121.0°, n^{24}_D 1.4531.

Anal. Calcd. for C_9H_{12}: C, 89.94; H, 10.06. Found: C, 89.82; H, 10.61.

The compound showed bands in the infrared at 3090(s), 3070 (m), 3010(s), 2980(s), 1840(w), 1615(s), 1405(s), 1048(w), 1000(s), 918(s), 697(s), and 652(w) cm.$^{-1}$ (neat, liquid).

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On the Instability of Methanesulfinyl Chloride

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A convenient preparative method[1] has made methanesulfinyl chloride, $CH_3S(O)Cl$ (I), and its homologs readily available. As work with I in our laboratory has continued, the instability of the compound has become increasingly evident. We have, for example, found it impossible to prepare samples of the compound entirely free of color. When a carefully purified sample is distilled under reduced pressure it appears to be colorless on leaving the condenser but a yellow color develops as the distillate accumulates in the receiver. On long standing the color deepens, hydrogen chloride is evolved, and ultimately a yellow solid precipitates. We also have observed that sulfinate esters prepared from I are always contaminated with traces of methanesulfonyl chloride.

The instability of I was emphasized when a 200-g. sample, sealed in a glass ampoule, exploded from internal gas pressure after standing on the laboratory shelf for several months. Our present practice is never to store samples of sulfinyl chlorides except under refrigeration.

The evidence indicates that the primary decomposition is a disproportionation into methanesulfonyl chloride (II) and methanesulfenyl chloride (III), the latter accounting for the yellow color.

$$\underset{\mathrm{I}}{2\,CH_3S(O)Cl} \longrightarrow \underset{\mathrm{II}}{CH_3SO_2Cl} + \underset{\mathrm{III}}{CH_3SCl}$$

The liberation of hydrogen chloride would result from a secondary reaction of III with itself to form a variety of products.[2]

Several attempts were made to demonstrate the disproportionation. Refluxing of I at atmospheric pressure leads to the formation of II but methanesulfenyl chloride is highly unstable at such elevated temperatures (140–160°) and decomposes with the formation of hydrogen chloride and other products. It was thought best, therefore, to duplicate the temperature conditions under which I had decomposed on standing and have an agent present which would trap the methanesulfenyl chloride (III) as soon as it might be formed. Cyclohexene was chosen as the trapping agent since it reacts with III to form 2-chlorocyclohexyl methyl sulfide.[3]

Experimental

Freshly distilled methanesulfinyl chloride (49.3 g., 0.5 mole) and dry cyclohexene (22.1 g., 0.27 mole) were sealed in a clear glass ampoule and allowed to stand on a window sill for 167 days. The mixture slowly turned dark brown in color, but there was no evidence of pressure development when the seal was broken periodically. When the mixture was finally removed and distilled under reduced pressure it yielded 12.9 g. (0.12 mole) of methanesulfonyl chloride (II) and 21.8 g. (0.13 mole) of 2-chlorocyclohexyl methyl sulfide (IV) and an unidentified dark residue.

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(2) E. Schneider, *Chem. Ber.*, **84**, 911 (1951).

(3) H. Böhme and H. J. Gran, *Ann.*, **577**, 68 (1952).