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: $\tau_2 = 4.20$, $\tau_3 = 4.97$, $\tau_4 = 5.01$; $J_{23(\text{cis})} = 9.0$, $J_{24(\text{trans})} = 17.5$, $J_{34} = 2.5$ 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.

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

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).

The infrared spectra of both II and IV were identical with those of authentic samples.

Acknowledgment.—We wish to thank the donors of the Petroleum Research Fund administered by the American Chemical Society for support of the research in the course of which the above observation was made.

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s-Triazines. I. Reaction of Vinylmagnesium Chloride with Cyanuric Chloride

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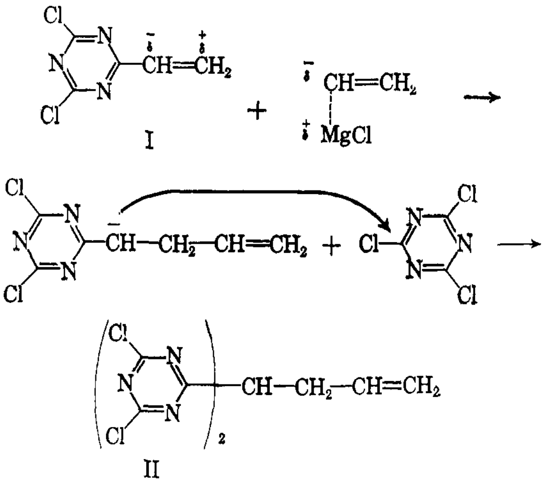
Condensation of alkylmagnesium halides with cyanuric chloride was reported to give 2-alkyl-4,6-dichloro-*s*-triazines.[2] When applied to vinylmagnesium chloride, this reaction could be expected to yield 2,4-dichloro-6-vinyl-*s*-triazine (I).

The reaction gave a product boiling at 198° (10 mm.), somewhat higher than expected for structure I. The elemental analysis of the crystallized product was in good agreement with I, but its molecular weight was double that of I.

The product showed an inflection in the ultraviolet at 255 mμ (cyclohexane) but no maximum. It exhibited infrared bands at 925 ($C{=}CH_2$ out of plane in phase deformation), 1852 (overtone of the deformation band), 1648 ($C{=}C$ stretching), and 980 cm.$^{-1}$ ($C{=}CH$ out of plane deformation), consistent with monosubstituted ethylene[3]; one at 1520 (triazine ring stretching) and a band at 848 cm.$^{-1}$, characteristic of a dichlorotriazine (*cf.* 2,4-dichloro-6-ethyl-*s* triazine,[4] showing corresponding bands at 1500 and 848 cm.$^{-1}$).

The n.m.r. spectrum was characteristic of a typical allyl group. The olefinic hydrogens formed an ABX pattern with AB ($=CH_2$) near 4.97 τ and X ($=CH-$) at 4.15 τ, with $J_{trans} \cong 17$ c.p.s., $J_{cis} \cong 9$ c.p.s. The four X lines were split further into triplets ($J = 6.6$ c.p.s.) due to coupling to the adjacent $-CH_2-$ group. The $-CH_2-$ resonance appeared at 6.91 τ as a triplet. Finally, at 5.48 τ, a one-proton 1-2-1 triplet ($J = 7.5$ c.p.s.) was observed. It was concluded that this absorption could be assigned to another CH hydrogen to which the CH_2 was also coupled. The entire spectrum is, therefore, consistent with the structure $CH_2{=}CH{-}CH_2\overset{|}{\underset{|}{C}}H$. A vinyl triazine, on the other hand, would be expected to show a typical vinyl spectrum of 12 to 15 lines in the 3.0- to 4.3-τ region, as has been observed in 2,4-dimethyl-6-vinyl-*s*-triazine[5] in these laboratories.

All the data are consistent with structure II, the formation of which can be rationalized as follows.



The original nucleophilic attack of vinyl anion on cyanuric chloride forms 2,4-dichloro-6-vinyl-*s*-triazine (I). The vinyl carbon in the 2-position would be much more electrophilic than the ring carbons in cyanuric chloride, and would undergo a very fast attack by a second molecule of the Grignard reagent. The resulting carbanion at the 1-position of the sidechain will now attack cyanuric chloride and produce II. An attack of the carbanion on I would give rise to high molecular weight by-products, which always accompanied product II.

It is not surprising that the great susceptibility of I to nucleophilic attack would preclude any accumulation of it in the reaction mixture. Indeed, even in reactions performed at −40°, in nonpolar media, in high dilution, and with other organometallic reagents (vinyllithium and tetravinyltin), no trace of the monomer (I) could be detected.

Experimental

1,1-Di(2′,4′-dichloro-1′,3′,5′-triazin-6′-yl)but-3-ene (II).—A solution of vinylmagnesium chloride (0.2 mole) in tetrahydrofuran (total volume 62.5 ml., 3.34 *N*) was added over an 8-min. period to a stirred solution of 18.44 g. (0.1 mole) of cyanuric chloride in 400 ml. of methylene dichloride at −30 to −15°. Stirring was continued at −15° for 1.5 hr., by which time a negative test with Gilman's reagent[6] was obtained. The very dark solution was decomposed at −30° by dropwise addition of 18 ml. of water, followed by addition of anhydrous magnesium sulfate (20 g.) and of diatomacious earth (10 g.). The solution was filtered, the cake was washed with methylene dichloride, and the solvent was evaporated under reduced pressure at 20°. The black residue was extracted with 200 ml. of pentane at 20°. The pentane solution was decolorized with charcoal, and the solvent was evaporated. The residue (16.7 g.) was estimated by its infrared and ultraviolet absorption to contain *ca.* 80% of II. Distillation gave (a) cyanuric chloride (4.3 g., 23.3%) which sublimed at 90° (11 mm.) and (b) product II (3.85 g., 21.9%), b.p. 198° (10 mm.), as a pale yellow oil which solidified at room temperature. The low recovery of distilled material was due to its polymerization during the distillation. Crystallization from pentane gave colorless rosettes of needles, m.p. 74.2–75.0° (cor.).

Anal. Calcd. for $C_{10}H_6Cl_4N_6$: C, 34.12; H, 1.72; Cl, 40.29; N, 23.87; mol. wt., 352.03. Found: C, 34.29; H, 1.89; Cl, 40.50; N, 23.89; mol. wt., 354.

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