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

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

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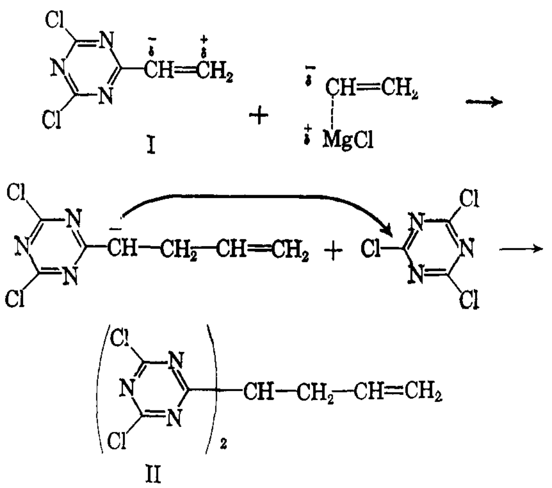
Condensation of alkylmagnesium halides with cyanuric chloride was reported to give 2-alkyl-4,6-dichloro-*s*-triazines.[2] When applied to vinylmagnesium chloride, this reaction could be expected to yield 2,4-dichloro-6-vinyl-*s*-triazine (I).

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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