equivalent of sodium hydroxide when the biguanide hydrochloride was used.

2-Amino-6-o-hydroxyphenyl-4-β-phenethylamino-s-triazine (Compound 9). A mixture of 4.8 g. (0.02 mole) of β-phenethylbiguanide hydrochloride in 15 ml. of methanol was treated with 5 ml. (0.02) mole of 23% sodium methoxide in methanol. The sodium chloride formed was separated and the filtrate on evaporation gave a residue of the biguanide free base which was granulated under pentane. The biguanide was suspended in 5 ml. (excess) of methyl salicylate and heated in an oil bath maintained at 115° for 20 min. with noted evolution of basic fumes. When cool, the formed sirup was granulated under pentane to give 5.49 g. (81%) of crude product.

Compounds 5–12 were similarly prepared.

Hydrogenation of compound 23. A mixture of 2.23 g. (0.0074 mole) of the compound in 2.46 ml. of 3*N* hydrochloric acid and 250 ml. of methanol, and 0.5 g. of 5% rhodium-on-carbon was hydrogenated in the Parr hydrogenator at 20° at an initial pressure of 62.5 lbs. of hydrogen. Within 10 min. the theoretical hydrogen (3 equivalents for reduction of nitro to amine group) was absorbed. After removal of the catalyst and evaporation of the solvent, there was obtained 2.17 g. (90%) of yellow crystals of 2-amino-4-*n*-amylamino-6 *m*-aminophenyl-*s*-triazine hydrochloride hydrate, m.p. 73–79°; recrystallized (water), m.p. 79–80°.

Anal. Calcd. for $C_{14}H_{23}ClN_6O$: C, 51.5; H, 7.1; N, 26.7. Found: C, 51.5; H, 7.2; N, 27.4.

The dipicrate melted at 201–203° (acetonitrile).

Anal. Calcd. for $C_{26}H_{24}N_{12}O_{14}$: C, 43.0; H, 3.3; N, 23.2. Found: C, 43.2; N, 3.8; N, 23.2.

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[CONTRIBUTION FROM RESEARCH AND DEVELOPMENT DIVISION, SPENCER CHEMICAL CO.]

Vinyl Isocyanurates. Preparation of Alkenyl Isocyanurates by Trimerization or Cotrimerization of Isocyanates

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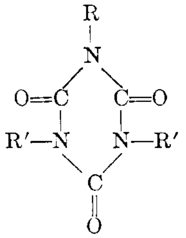
Trivinyl isocyanurate was obtained from the trimerization of vinyl isocyanate. Cotrimerizations of vinyl or allyl isocyanates with alkyl or aryl isocyanates yielded the corresponding unsymmetrically substituted isocyanurates. Effects of catalysts and reactant ratios on the trimerization reactions were studied.

A number of examples are to be found in the literature describing the preparation of isocyanurates by trimerization of aromatic and aliphatic isocyanates.[1,2] The trimerization of cyanic acid to form cyanuric acid is also known.[3] No examples could be found for the preparation of alkenyl isocyanurates by this type of reaction. The most nearly analogous method for the synthesis of an unsaturated derivative is that involving reaction of potassium isocyanate with allyl chloride to produce triallyl isocyanurate.[4]

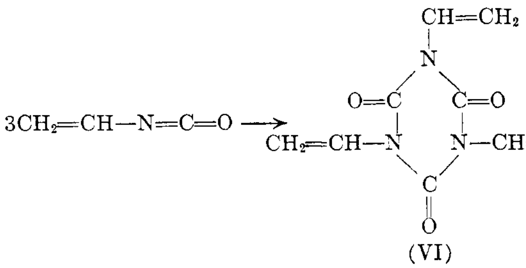
Vinyl isocyanurate is reported to result from cleavage of triallyl isocyanurate in the presence of a phenol.[5] The product was not fully described or characterized, and we were not able to repeat this reaction in our laboratory. The syntheses of di- and triallyl compounds have been effected by reaction of cyanuric acid with allyl chloride in aqueous caustic.[6] The mono- and diallyl derivatives are reported to be obtained from reaction of the triallyl compound with phenol and aromatic solvents in the presence of various catalysts.[7] Isocyanurates bearing both saturated and unsaturated aliphatic substituents have not been reported.

We have found that mixed trisubstituted isocyanurates of the following types can be prepared by base-catalyzed cotrimerization of the appropriate isocyanates.



I. R = $-CH=CH_2$; R′ = $-C_4H_9$
II. R = $-CH_2-CH=CH_2$; R′ = $-C_2H_5$
III. R = $-C_2H_5$; R′ = $-CH_2-CH=CH_2$
IV. R = $-C_4H_9$; R′ = $-CH=CH_2$
V. R = $-C_6H_5$; R′ = $-CH=CH_2$

Homotrimerization of vinyl isocyanate has also provided the novel trivinyl isocyanurate (VI) in good yield:



(VI)

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[1] A. W. Hofman, *Ber.*, **18**, 765 (1885); I. C. Kogon, U. S. Pat. **2,838,511** (1958).

[2] E. M. Smolin and L. Rapoport, *Heterocyclic Compounds*, Interscience, New York, 1959, p. 104; Australian Pat. **45,955** (1959).

[3] P. Klason, *J. prakt. Chem.*, (2), **33**, 129 (1886).

[4] D. W. Kaiser and D. H. Church, U. S. Pat. **2,536,849** (1951).

[5] H. Meis and H. Sauer, U. S. Pat. **2,860,139** (1958).

[6] B. E. Lloyd and F. L. Kelly, U. S. Pat. **2,894,950** (1959); T. C. Frazier *et al.*, *J. Org. Chem.*, **25**, 1944 (1960).

The vinyl isocyanate prepared for use in these reactions appeared to have rather limited storage stability and was prone to polymerize even when stored in the cold in the presence of dinitrobenzene inhibitor. Polymeric material also formed readily on condensing surfaces during distillation of this isocyanate. The polymer was not completely characterized, but was indicated by infrared absorption spectra to be a linear polyuret with limited cross linking through vinyl polymerization.

Cotrimerization reactions which produce liquid reaction mixtures present difficult separation problems. Most mixtures were readily resolved by gas-liquid chromatography on silicone grease with firebrick or red chromosorb support. The major product could generally be controlled by proper adjustment of reactant ratios. Statistical mixtures are not necessarily obtained, apparently because of an imbalance in relative reactivities of the various isocyanates. Thus vinyl isocyanate, which has a pronounced tendency towards homotrimerization, reacted with two moles of butyl isocyanate to produce principally butyldivinyl isocyanurate. The use of reversed proportions resulted in about equal quantities of the trivinyl and butyldivinyl derivatives. Reactions of phenyl isocyanate with vinyl isocyanate yielded predominantly triphenyl isocyanurate along with some dimer, 1,3-diphenyl-1,3-diazacyclobutane-2,4-dione, and the divinylphenyl compound. Predominance of the triphenyl compound was unexpected in view of the general use of the phosphine catalyst for preparation of the dimer. A lesser degree of selectivity was noted in reactions of allyl isocyanate with ethyl isocyanate, in that the principal product was the one expected from the reactant ratios. Thus diallylethyl isocyanurate was readily obtained as the major product by use of the corresponding proportions of reactants.

Both triethylamine and triethylphosphine are suitable catalysts for trimerization of vinyl isocyanate. However, with the less reactive methylene homolog, allyl isocyanate, only the phosphine catalyst was effective in either homo- or cotrimerizations. An attempt to promote the reaction of allyl isocyanate with ethyl isocyanate by use of the amine with added ethanol to form an amine-carbamate catalyst system was not successful. This procedure has been recommended for use with aliphatic isocyanates which do not trimerize with tertiary amines alone.[8]

EXPERIMENTAL[9]

Liquid mixtures of isocyanurates obtained in the cotrimerization reactions were separated by a 2-meter chromatographic column one and a quarter inch in diameter packed with silicone grease on firebrick. The column temperature was 175° and the helium flow rate was 1100 cc. per minute. Sample sizes of 1 ml. were used, and products were trapped at salt-ice bath temperatures. Only the major peaks obtained by gas chromatography were investigated. The fractions collected were rechromatographed through silicone grease on red chromosorb to establish purity.

Starting materials. Triethylphosphine. Triethylphosphine was obtained from the Grignard reaction in a modification of the procedure of Hibbert who isolated this material as its carbon disulfide adduct.[10] By continued heating of the Grignard reaction mixture to insure distillation of all triethylphosphine, and removal of the ether with an efficient fractionating column, the phosphine was obtained in 66% yield, 122–125°. Alternatively, an acid extraction as described by Slotta can be used.[11]

Allyl isocyanate. This compound was prepared in 94% yield by the method of Cahours.[12]

Vinyl isocyanate; polymer formation. This isocyanate was prepared by the procedure of Hart with a slight modification.[13] No vinyl isocyanate was removed during the course of the reaction. After the reaction was complete, all material distilling up to 85° was collected. Fractionation of this material gave vinyl isocyanate in 65% yield, b.p. 40–43°.

Refluxing vinyl isocyanate through an efficient column filled with glass beads led to a gradual buildup of a hard white solid on a cold finger at the top of the column. This solid does not melt up to 300°, is insoluble in common organic solvents and appears to be a polymer of vinyl isocyanate.

Anal. Calcd. for $(C_3H_3NO)_x$: C, 52.17; H, 4.35; N, 20.29. Found: C, 51.83; H, 4.33; N, 20.71.

Infrared analysis of the polymer sample in a potassium bromide disk showed a strong carbonyl peak (5.8 μ) and only a trace of isocyanate (4.4 μ), indicating polymerization of the isocyanate group. A strong vinyl peak (6.1 μ) was present, and some crosslinking through vinyl polymerization was possibly indicated by peaks at 7.0 μ and 7.5 μ. The solid appears to be a linear polyuret with a limited amount of cross linking through vinyl polymerization.

Trimerization of vinyl isocyanate and isolation of trivinyl isocyanurate. Freshly prepared vinyl isocyanate (10.35 g., 0.15 mole) was distilled into a reaction flask for separation from the dinitrobenzene inhibitor. The flask was immersed in an ice bath, and triethyl phosphine (1.49 g., 0.0126 mole) was added with stirring. A momentary vigorous reaction caused flooding of the one-foot condenser. (The reaction can be moderated by use of a Dry Ice bath instead of an ice bath.) The mixture was allowed to come very slowly to room temperature, and 2 hr. after the catalyst addition an infrared spectrum of the reaction mixture was taken. This spectrum indicated complete conversion of vinyl isocyanate to trivinyl isocyanurate; particularly significant was the disappearance of the isocyanate peak and the appearance of peaks for the isocyanurate ring. Inhibitors (0.1 g. hydroquinone and 0.1 g. dinitrobenzene) were added. The triethylphosphine was recovered by distillation at room temperature under reduced pressure, and the product (5.73 g., 55.4% yield) was distilled as a light yellow liquid at about 127°/0.28 mm. This material was carefully fractionated, b.p. 114–116°/0.17 mm. The trivinyl isocyanurate solidified on cooling and scratching. After drying, a white solid, m.p. 32–34°, remained. The infrared spectrum was identical to that of the initial distillate. When the solid was remelted it was colorless, indicating the original yellow tinge was due to trace impurities.

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(7) H. Meis and H. Saur, U. S. Pat. 2,830,051 (1958).

(8) E. Windemuth *et al.*, German Pat. 1,013,869 (1957).

(9) All reactions of isocyanates were carried out under an atmosphere of dry nitrogen. Isocyanates were freshly distilled prior to use. Melting points and boiling points are uncorrected.

(10) H. Hibbert, *Ber.*, **39**, 161 (1906).

(11) K. Slotta and R. Tschesche, *Ber.*, **60**, 298 (1927).

(12) A. Cahours, *Ann.*, **102**, 297 (1857).

(13) R. Hart, *Bull. Soc. Chim. Belg.*, **65**, 291 (1956).

Anal. Calcd. for $C_9H_9N_3O_3$: C, 52.17; H, 4.38; Iodine number, 368; m.w. 207. Found: C, 52.22; H, 4.32; Iodine number, 375; m.w. 197.

The infrared spectrum of this compound showed carbonyl (5.8 μ), terminal vinyl (6.05, 10.30, and 10.95 μ) and isocyanurate (13.01 μ) peaks.

Triethylamine was used in place of triethylphosphine to provide trivinyl isocyanurate from vinyl isocyanate. The reaction was conducted in the same manner as that described with triethylphosphine. Infrared analysis indicated completeness of reaction, and the entire reaction mixture distilled as product, leaving only a trace of residue in the distillation flask.

It was found that the presence of dinitrobenzene inhibitor does not prevent homotrimerization. This is a significant advantage in view of the air sensitivity of uninhibited vinyl isocyanate.

Cotrimerization of allyl isocyanate with one-half mole of ethyl isocyanate. Effect of catalysts. Freshly distilled allyl isocyanate (17 g., 0.205 mole) and ethyl isocyanate (7.33 g., 0.103 mole) were mixed with stirring. The reaction was followed spectroscopically while catalysts were added consecutively in order to follow their catalytic influence.

Neither triethylamine nor a mixture of triethylamine and carbamates was effective as catalyst, but triethylphosphine was quite effective over a long reflux period. Thus, after addition of triethyl amine (2.55 g., 0.025 mole) and refluxing 1 hr., the infrared spectrum of the reaction mixture failed to show the appearance of isocyanurate or carbonyl peaks and showed strong isocyanate absorption. Addition of ethanol (0.24 g.) to form a carbamate, followed by 1 hr. of reflux, failed to change the spectrum. Refluxing with triethylphosphine (2.98 g., 0.025 mole), however, caused gradual disappearance of the isocyanate peak and an appearance of the isocyanurate peaks (5.8 and 13.0 μ). After 11 hr. of reflux, the reaction was essentially complete.

The volatile materials were removed under 1 mm. vacuum at room temperature over 2–3 hr. to give 5.4 g. of colorless liquid containing catalysts and unchanged isocyanates.

The mixture of isocyanurates was distilled over a range of about 84–107° at 0.25–0.30 mm. The total yield was 16.5 g. or 68% if calculated as diallylethyl isocyanurate. This distillate was separated by gas-liquid chromatography into its major peaks, which were collected.

The first compound eluted by gas-liquid chromatography was triethyl isocyanurate, consisting of approximately 6% of the distillate. It was eluted as a liquid and after standing in an ice box overnight, crystallized to a solid melting at 84–87°. After recrystallization from ethanol, the melting point was 92–94° (reported 95°).[14] On infrared examination, the compound showed peaks for isocyanurate and for carbonyl but did not show peaks for terminal unsaturation which were found in all other products (allyl isocyanurates) eluted later and described below.

The second main product eluted was allyldiethyl isocyanurate, representing about 20% of the distillate.

Anal. Calcd. for $C_{10}H_{15}N_3O_3$: C, 53.27; H, 6.71; Iodine number, 113. Found: C, 53.40; H, 6.77; Iodine number, 114.

Only a very small sample remained for refractive index determination, which because of the size of the sample was not too distinct, n_D^{26} 1.4910.

The third major product eluted, comprising 35% of the distillate, was diallylethyl isocyanurate, n_D^{26} 1.5013.

Anal. Calcd. for $C_{11}H_{15}N_3O_3$: C, 55.68; H, 6.37; Iodine number, 214. Found: C, 55.68; H, 6.24; Iodine number, 210.

The final major product eluted, representing about 22% of the distillate, was triallyl isocyanurate.

Anal. Calcd. for $C_{12}H_{15}N_3O_3$: C, 57.80; H, 6.06; Iodine number, 306. Found: C, 57.61; H, 5.93; Iodine number, 299.

The constitution of this product was also confirmed by the fact that its retention time and infrared spectrum were the same as an authentic sample of triallyl isocyanurate prepared by the method of Lloyd.[6]

Cotrimerization of butyl isocyanate with one-half mole of vinyl isocyanate. Isolation of butyldivinyl isocyanurate as the major product. To freshly distilled vinyl isocyanate (5.87 g., 0.085 mole) and butyl isocyanate (17.0 g., 0.17 mole) was added triethylphosphine (1.12 g., 0.095 mole) while stirring. The initial exothermic reaction was moderated by cooling in an ice bath. The resulting dark mixture was then refluxed for about 5 hr.

The volatile materials were removed at 1 mm. at room temperature over a period of about 5 hr.

The product was distilled and collected over a wide range, 120° at 0.39 mm. to 155° at 0.32 mm. The total yield was 17.0 g. or 74% if calculated as dibutylvinyl isocyanurate. This was separated by gas-liquid chromatography into four main peaks. The isolated fractions were passed through a more sensitive, smaller gas-liquid chromatograph column and, thereby, shown to be pure compounds.

The infrared data were consistent for these compounds. All of the compounds showed peaks for isocyanurate and for carbonyl. The last major product eluted, tributyl isocyanurate, did not show peaks for unsaturation as found in the three vinyl isocyanurates eluted before this compound.

The first major product eluted was trivinyl isocyanurate, representing 16% of the distillate.

Anal.[15] Calcd. for $C_9H_9N_3O_3$: C, 52.17; Iodine number, 367. Found: C, 52.45; Iodine number, 353.

The infrared spectrum and the retention time of the isolated trivinyl isocyanurate was the same as the sample of this material obtained by trimerization of vinyl isocyanate.

The second product, butyldivinyl isocyanurate, eluted was the major product, n_D^{27} 1.5136, representing 48% of the distillate.

Anal. Calcd. for $C_{11}H_{15}N_3O_3$: C, 55.68; H, 6.37; Iodine number, 214. Found: C, 55.65; H, 6.47; Iodine number, 204.

The third product eluted was dibutylvinyl isocyanurate and represented 11% of the distillate.

Anal. Calcd. for $C_{13}H_{21}N_3O_3$: C, 58.03; Iodine number, 95. Found: C, 58.18; Iodine number, 99.

The final product, tributyl isocyanurate, eluted represented 19% of the distillate.

Anal. Calcd. for $C_{15}H_{27}N_3O_3$: C, 60.58; Iodine number, O. Found: C, 60.37; Iodine number, 8.

Cotrimerization of vinyl isocyanate with one-half mole of butyl isocyanate. Isolation of butyldivinyl isocyanurate and trivinyl isocyanurate as the major products. Freshly distilled vinyl isocyanate (6.91 g., 0.10 mole) and butyl isocyanate 4.95 g., 0.05 mole) were stirred together at -45° to −50° while triethylphosphine (1.49 g., 0.0126 mole) was added. An infrared spectrum taken after the mixture was allowed to come to room temperature showed evidence of the presence of the product as well as a small amount of unchanged isocyanates. The mixture was then heated at 100° for about 4 hr., after which no evidence for the presence of unreacted isocyanates was shown by infrared analysis.

The catalyst was removed at 1 mm. at room temperature over a period of 3 hr. The product was then distilled at 112–113°/0.20–0.21 mm. The yield was 7.30 g., or 62%, if calculated as butyldivinyl isocyanurate.

By gas-liquid chromatographic separation, this distillate was shown to contain approximately 50% trivinyl isocyanurate, 45% butyldivinyl isocyanurate, and 5% dibutylvinyl isocyanurate, eluted in this order. These products were

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[14] E. M. Smolin and L. Rapoport, *Heterocyclic Compounds*, Interscience, New York, 1959, p. 404.

[15] Hydrogen analyses obtained were found to be in error when this series of compounds was run because of a poor water absorption train discovered later by analysis of known compounds. Only butyldivinyl isocyanurate was available in sufficient quantity to repeat the analysis.

isolated, passed through a more sensitive, smaller gas-liquid chromatograph column and, thereby, shown to be pure compounds by the production of single peaks. The compounds were identified by showing that their retention times and infrared spectra were identical with the corresponding compounds obtained as described in the previous experiment.

Divinylphenyl isocyanurate from the reaction of one-half mole of vinyl isocyanate with phenyl isocyanate. Freshly distilled vinyl isocyanate (3.45 g., 0.05 mole) and phenyl isocyanate (11.91 g., 0.10 mole) were stirred together while triethylphosphine (1.49 g., 0.0126 mole) was added. A white precipitate formed. The mixture then became very hot, the solid redissolved, and the solution turned deep red. The entire mass resolidified when allowed to stand overnight. The mixture was then taken up in chloroform and chilled to −40°, to precipitate triphenyl isocyanurate (5.70 g.), m.p. 280–281°. The infrared spectrum was consistent for this compound.

Residual solids obtained on evaporation of the chloroform were chromatographed on an alumina column in 1:1 chloroform–carbon tetrachloride to give 1 g. (19% yield based on vinyl isocyanate) of white solid whose infrared spectrum showed terminal vinyl, phenyl and carbonyl peaks as well as a peak for the isocyanurate group. After recrystallization from ether, the divinylphenyl isocyanurate melted at 115–116°.

Anal. Calcd. for $C_{13}H_{11}N_3O_3$: C, 60.70; H, 4.31; N, 16.34. Found: C, 60.76; H, 4.11; N, 16.62.

The above reaction was repeated while cooling in a salt-ice bath during the addition of a relatively smaller amount of triethylphosphine. After the phenyl isocyanate (10.21 g., 0.086 mole), vinyl isocyanate (3.0 g., 0.043 mole), and triethylphosphine (0.27 g., 0.0022 mole) were mixed, a yellow solid formed which did not redissolve. In this case, on attempted solution of the reaction mixture in chloroform, some less soluble solid (about 0.5 g., m.p. 185–186°) was isolated. This compound was 1,3-diphenyl-1,3-diazacyclobutane-2,4-dione, the dimer of phenyl isocyanate. After recrystallization from chloroform, fine white platelets, m.p. 185–186°, were obtained.

Anal. Calcd. for $C_{14}H_{10}N_2O_2$: C, 70.58; H, 4.23. Found: C, 70.42; H, 4.40. This 4-membered ring compound showed carbonyl absorption at a lower wavelength (5.63 μ) than obtained for the isocyanurates.

An authentic sample of 1,3-diphenyl-1,3-diazacyclobutane-2,4-dione was prepared by addition of a few drops of triethylphosphine to phenyl isocyanate according to the procedure of Hofman.[16] This material melted at 185–186° after recrystallization from chloroform or from ether. The melting point and infrared spectrum were identical with that of the compound described above.

By chilling the remaining chloroform solution to −60°, triphenyl isocyanurate (5.0 g., m.p. 280–281°) was obtained. In this experiment as well as the one run at room temperature, the major product appears to be the isocyanurate from the homotrimerization of phenyl isocyanate.

The solids obtained on evaporation of the remaining chloroform solution were recrystallized from ether to yield a third product, divinylphenyl isocyanurate (2.0 g., 35% yield based on vinyl isocyanate), which after a second recrystallization melted at 116–117°. This material was the same as that obtained in the analogous experiment carried out at room temperature as indicated by melting point, mixture melting point, and identity of spectra. No attempt was made to isolate trivinyl isocyanurate in these reactions.

Cotrimerization of vinyl isocyanate with one-half mole of ethyl isocyanate. Freshly distilled vinyl isocyanate (6.91 g., 0.10 mole) and ethyl isocyanate (3.55 g., 0.05 mole) in 50 ml. of benzene (dried over sodium) were cotrimerized by addition of triethylphosphine (1.49 g., 0.0126 mole) followed by a 5-hr. reflux period. After removal of benzene, triethylphosphine, and any unchanged isocyanates under vacuum at room temperature, the product was distilled at 128–129°/0.33–0.35 mm. giving 7.00 g. (67% yield based on the formation of divinylethyl isocyanurate) of a faintly yellow liquid.

Infrared analysis of the distillate indicates that isocyanurates containing ethyl and vinyl groups were formed. Gas-liquid chromatographic separation failed with the absorbent used but showed that trivinyl isocyanurate as well as very closely boiling and similarly adsorbed materials, probably including divinylethyl isocyanurate, were formed. Elemental analysis and iodine number could also be consistent with this view, as can be seen when the calculated values for trivinyl isocyanurate and divinylethyl isocyanurate shown below are compared with the values obtained. On the basis of the past experience in cotrimerizations with vinyl isocyanate and difficulty in chromatographically separating the products, it seems that these products are more likely than a mixture of trivinyl and triethyl isocyanurates.

Anal. Calcd. for $C_9H_9N_3O_3$: C, 52.17; H, 4.38; Iodine number, 367. Calcd. for $C_9H_{11}N_3O_3$: C, 51.67; H, 5.30; Iodine number, 242. Found: C, 52.02; H, 5.05; Iodine number, 296.

Assuming that trivinyl isocyanurate and divinylethyl isocyanurate were the major products, the iodine number indicates that the percents of these compounds were 43 and 57%, respectively. No further work was done to establish these views.

Acknowledgment. We are indebted to W. Vanderlinde for his technical assistance and K. J. Bombaugh, W. E. Thomason, and C. E. Cook for the gas-liquid chromatographic separations.

MERRIAM, KAN.

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(16) A. W. Hofman, *Ber.*, **18**, 764 (1885).