into water. The solid which separated was collected and crystallized from benzene–petroleum ether to give pure **12** (0.2 g): mp 146–148°; ir, λ_{max} 2.97, 3.05, 5.85, 5.90 (sh), 6.41, 6.75, 8.10, 8.51, 9.39, 13.16 μ; for nmr, see text.

Anal. Calcd for $C_{15}H_{14}N_2O_3$: C, 66.65; H, 5.22; N, 10.37. Found: C, 66.63; H, 5.27; N, 10.54.

B. From 10.—Treatment of **10** with zinc in acetic acid as described for **11** gave N-mandelyl-N′-phenylurea (**12**) in 75% yield.

Oxidation of 12 to 10.—To a cooled solution of **12** (0.27 g) in acetone (10 ml) was slowly added an 8 *N* solution of CrO_3[19] (2.0 ml). The mixture was heated 5 min at 50°, then was poured into cold water. The solid which separated (0.15 g) was identified as **10**.

3-Benzyl-5-benzyloxy-1,5-diphenylhydantoin (13). A. From 6a.—A solution of **6a** (0.5 g) in benzylamine (10 ml) was heated 6 hr at 175°, then was poured into water (50 ml). The yellow oil which separated was extracted several times with hot petroleum ether. The combined extracts were washed with dilute HCl and water, dried ($MgSO_4$), and evaporated to yield 0.3 g of **13**: mp 121–123° after crystallization from benzene–petroleum ether; ir, λ_{CO} 5.62, 5.81 μ.

Anal. Calcd for $C_{29}H_{24}N_2O_3$: C, 77.66; H, 5.39; N, 6.25. Found: C, 77.51; H, 5.52; N, 6.41.

B. From 9.—To a solution of **9** (0.1 g) and benzyl chloride (0.1 g) in 95% ethanol (7.0 ml) was added a 0.11 *N* solution of KOH in ethanol (2.7 ml). The mixture was refluxed 2 hr; then it was diluted with water and extracted with ether. The dried ($MgSO_4$) ethereal extract was evaporated to give a residue which solidified on trituration with ethanol. This product (80 mg) was crystallized from benzene–petroleum ether to give pure **13**.

(19) C. Djerassi, R. R. Engle, and A. Bowers, *J. Org. Chem.*, **21**, 1547 (1956).

Registry No.—**6a**, 16710-18-2; **6b**, 16710-19-3; **6c**, 16710-20-6; **7a**, 16710-21-7; **7b**, 16710-22-8; **8**, 16710-23-9; **9**, 16710-24-0; **10**, 15903-38-5; **11**, 16710-26-2; **12**, 16710-27-3; **13**, 16709-72-1; **16**, 16709-73-2; **17**, 16709-74-3.

Synthesis and Reactions of "Anhydrochloralurethans"

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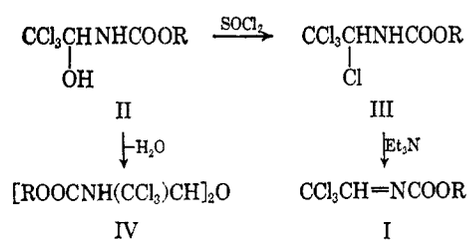
The previously unreported anhydrochloralurethans (I) are obtained by dehydrochlorination of alkyl 1,2,2,2-tetrachloroethylcarbamates (III). Reaction of I with water, alcohols, and amines affords chloral O,N- and N,N-acetals. The latter compounds are also produced in the reaction of chloralurethans (II) with alkyl and aryl isocyanates. Treatment of II and III with carbonyl chloride in the presence of N,N-dimethylformamide as the catalyst gives rise to the formation of 1,2,2,2-tetrachloroethyl isocyanate (XI), which undergoes the Michalis–Arbuzov reaction with triethyl phosphite to afford diethyl 1-isocyanato-2,2,2-trichloroethylphosphonate (XII).

The synthesis of "anhydrochloralurethans" (I) was reported in 1891 by Moscheles.[1] However, Feist[2] had shown later that the compounds, isolated by Moscheles, had structure IV rather than I. In view of the anticipated reactivity of the imines I with regard to addition to the activated double bond, we attempted their synthesis from chloralurethans (II).[3] Since dehydration led to the formation of IV,[1,2] most likely *via* addition of unreacted II to the generated I, we selected a dehydrochlorination procedure.

Heating of chloralurethans (II) with thionyl chloride affords alkyl 1,2,2,2-tetrachloroethylcarbamates (III) in high yield (Scheme I). The dehydrochlorination of III in benzene, using triethylamine as the hydrogen chloride acceptor, proceeds at room temperature, and the previously unreported "anhydrochloralurethans" I are thus obtained in 40–50% yield of distilled product.

SCHEME I



The imines I are colorless liquids which darken on standing. Their structure was verified by elementary analysis, infrared ($\nu_{C=O}$ 1745 cm^{-1}, $\nu_{C=N}$ 1669 cm^{-1}) and nmr spectroscopy. For example, I (R = C_2H_5) shows the following signals (50% CCl_4, relative to TMS): singlet at 8.2 ppm, quartet at 4.3 ppm, and triplet at 1.38 ppm, with a relative intensity ratio of 1:2:3.

Likewise, ethyl 1-chloro-2,2,2-tribromoethylcarbamates obtained from ethyl 1-hydroxy-2,2,2-tribromoethylcarbamate[3] and thionyl chloride can be dehydrochlorinated to C-tribromomethyl-N-carboethoxyazomethine (V), as evidenced by infrared and nmr spectroscopy. However, the imine V is heat sensitive, and purification by vacuum distillation is not possible.[4,5]

The reactivity of the C=N double bond in I is evidenced by rapid and exothermic addition of water, alcohols, and amines to yield the corresponding hemiacetals II, O,N-acetals VI, and N,N-acetals VII (Scheme II). However, addition of hydrogen phosphite to afford the 1:1 adduct VIII is quite sluggish and requires the use of a base catalyst. For N-aroyl imines a similar activation of the C=N double bond toward addition of nucleophiles has been observed recently.[6]

The chloro group adjacent to nitrogen in alkyl 1,2,2,2-

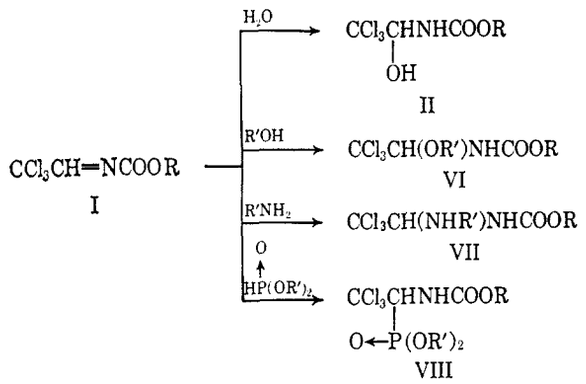
(1) R. Moscheles, *Ber.*, **24**, 1803 (1891).
(2) F. Feist, *ibid.*, **45**, 945 (1912).
(3) C. Bischoff, *ibid.*, **7**, 628 (1874).

(4) After completion of our investigation the *in situ* generation of I (R = $CH_2C_6H_5$) has been described, but purification by vacuum distillation was not possible because of heat sensitivity.[5]

(5) F. Weygand, W. Steglich, I. Lengyel, F. Fraunberger, A. Maierhofer, and W. Oettmeier, *Chem. Ber.*, **99**, 1944 (1966).

(6) S. W. Breuer, T. Bernath, and D. Ben-Ishai, *Tetrahedron Lett.*, 4569 (1966).

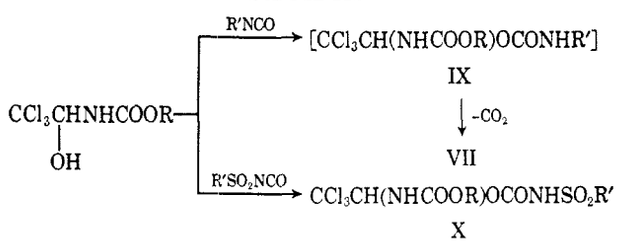
SCHEME II



tetrachloroethylcarbamates (III) undergoes rapid nucleophilic substitution and participates readily in the Michaelis–Arbuzov reaction. Therefore compounds II, VI, VII, and VIII can also be obtained from III. However, the reactions of III with water, alcohols, and amines may proceed by an elimination–addition sequence, involving I as the intermediate.

The N,N-acetals VII are also obtained in the base-catalyzed reaction of II with alkyl and aryl isocyanates. The initially formed 1:1 adducts IX undergo rapid elimination of carbon dioxide with formation of VII. In contrast, reaction of II with tosyl isocyanate results in the formation of the expected carbamate X (Scheme III).

SCHEME III



The elimination of carbon dioxide in the reaction of chloralamides with alkyl and aryl isocyanates has been observed recently,[7] while chlorosulfonyl isocyanate undergoes reaction with dialkyl 1-hydroxy-2,2,2-trichloroethylphosphonates to afford the expected 1:1 adducts.[8] Thus, a general trend is observed in the reaction of the chloral hemiacetalic hydroxy groups with alkyl, aryl, and sulfonyl isocyanates.

Since chloralurethans are readily available, we attempted conversion of the carbamate group into an isocyanate function, using carbonyl chloride as the attacking species. In the case of II simultaneous conversion of the hydroxy group into a chloro group was anticipated. While previously phosphorus pentachloride[9] and pyrocatechol–phosphorus trichloride[10] have been used to convert carbamates into isocyanates, carbonyl chloride does not undergo reaction with carbamates even at temperatures above 100°. However, addition of a catalytic amount of N,N-dimethylformamide achieves rapid conversion.[11]

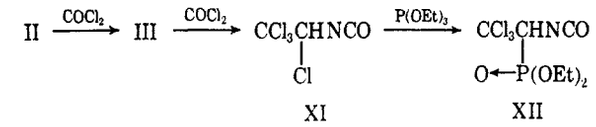
(7) A. Doerken and G. Schrader, German Patent 1,186,467 (1965); *Chem. Abstr.*, **62**, 16,149 (1965).

(8) H. Timmler, R. Wegler, and G. Unterstenhöfer, French Patent 1,403,523 (1965); *Chem. Abstr.*, **64**, 15,925 (1966).

(9) O. Folin, *Amer. Chem. J.*, **19**, 323 (1897).

(10) H. Gross and J. Gloede, *Chem. Ber.*, **96**, 1387 (1963).

Thus, simultaneous addition of carbonyl chloride and DMF to II or III in toluene or chlorobenzene affords 1,2,2,2-tetrachloroethyl isocyanate (XI), which



had been previously obtained in the reaction of 1-hydroxy-2,2,2-trichloroethyl isocyanate and thionyl chloride.[12] The chloro group adjacent to nitrogen is quite mobile and treatment of XI with triethyl phosphite results in the formation of the isocyanatophosphonate XII. Addition of alcohol to isocyanatophosphonates affords the carbamates VIII, identical with the compounds obtained from I and dialkylhydrogen phosphite and III and trialkyl phosphite.

The mechanism of formation of XI in the reaction of the carbamates II and III with carbonyl chloride involves the corresponding chloroformimidate as the intermediate.[11]

Experimental Section[13]

Methyl 1,2,2,2-Tetrachloroethylcarbamate (III, R = CH_3).—To a suspension of 222.5 g (1 mol) of methyl 1-hydroxy-2,2,2-trichloroethylcarbamate in 1200 ml of methylene chloride 119 g (1 mol) of thionyl chloride, containing 2.2 g of pyridine, is added. After refluxing for 60 min a clear solution is obtained and evaporation of the solvent affords 240 g (99.5%) of methyl 1,2,2,2-tetrachloroethylcarbamate, mp 91–92° (lit.[14] mp 90–91°) after recrystallization from carbon tetrachloride.

Anal. Calcd for $C_4H_5Cl_4NO_2$: C, 19.94; H, 2.09; N, 5.81. Found: C, 20.13; H, 1.97; N, 5.65.

In a similar manner **ethyl 1,2,2,2-tetrachloroethylcarbamate (III, R = C_2H_5** [mp 60–62° (lit.[14] mp 62–63°)], yield 97.3%], and **ethyl 1-chloro-2,2,2-tribromoethylcarbamate** (mp 77–78°, yield 96.4%) was obtained.

Anal. Calcd for $C_5H_7Br_3ClNO_2$: N, 3.60. Found: N, 3.60.

C-Trichloromethyl-N-carbomethoxyazomethine (I, R = CH_3).—To a solution of 20.2 g (0.02 mol) of triethylamine in 200 ml of benzene dropwise and with stirring 48.2 g (0.2 mol) of methyl 1,2,2,2-tetrachloroethylcarbamate in 200 ml of benzene is added over a period of 20 min at 25–40°. After cooling and removal of triethylamine hydrochloride by filtration the benzene is evaporated and vacuum distillation of the residue affords 16.7 g (40.7%) of C-trichloromethyl-N-carbomethoxyazomethine, bp 41–42° (0.1 mm).

Anal. Calcd for $C_4H_4Cl_3NO_2$: C, 23.50; H, 1.97; N, 6.85. Found: C, 23.62; H, 2.03; N, 7.02.

In a similar manner **C-trichloromethyl-N-carbethoxyazomethine (I, R = C_2H_5** [bp 70° (1.1 mm), yield 47.7%] was obtained.

Anal. Calcd for $C_5H_6Cl_3NO_2$: C, 27.73; H, 2.78; N, 6.56. Found: C, 27.92; H, 2.75; N, 6.83.

Reaction with Water.—Addition of I, R = C_2H_5, to aqueous acetone and evaporation of the acetone affords **ethyl 1-hydroxy-2,2,2-trichloroethylcarbamate (II, R = C_2H_5)**, mp 103° (lit.[3] mp 103°), in quantitative yield.

Reaction with Methanol.—The amount of 1.09 g (0.005 mol) of C-trichloromethyl-N-carbethoxyazomethine is added to excess methanol (5 ml). An immediate exothermic reaction occurs and evaporation of the methanol affords 1.12 g (90%)

(11) H. Ulrich, B. Tucker, and A. A. R. Sayigh, *Angew. Chem. Intern. Ed. Engl.*, **6**, 636 (1967).

(12) F. W. Hoover, H. B. Stevenson, and H. S. Rothrock, *J. Org. Chem.*, **28**, 1825 (1963).

(13) Analyses were by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Infrared spectra were determined in chloroform solution, using a Beckman IR-8 spectrophotometer. Nmr spectra were obtained from samples in deuteriochloroform solution on a Varian A-60 instrument using tetramethylsilane as the internal standard.

(14) M. Pianka and J. D. Edwards, British Patent 993,051 (1965); *Chem. Abstr.*, **63**, 9822 (1965).

of **ethyl 1-methoxy-2,2,2-trichloroethylcarbamate** (**VI**, **R** = C_2H_5, **R′** = CH_3O), mp 59–61° (lit.[12] mp 64–65°).

Reaction with Aniline.—To 1.09 g (0.005 mol) of C-trichloromethyl-N-carbethoxyazomethine in 15 ml of carbon tetrachloride 0.465 g (0.005 mol) of aniline is added. An immediate exothermic reaction occurs and evaporation of the solvent affords 1.56 g (100%) of **ethyl 1-phenylamino-2,2,2-trichloroethylcarbamate** (**VII**, **R** = C_2H_5, **R′** = C_6H_5), mp 85–87° after recrystallization from aqueous methanol.

Anal. Calcd for $C_{11}H_{13}Cl_3N_2O_2$: C, 42.41; H, 4.20; N, 8.99. Found: C, 42.40; H, 4.13; N, 9.14.

C-Tribromoethyl-N-carbethoxyazomethine (**V**).—To a solution of 7.7 g (0.02 mol) of ethyl 1-chloro-2,2,2-tribromoethylcarbamate in 70 ml of benzene with stirring and dropwise 2.22 g (0.022 mol) of triethylamine is added over a period of 3 min at 25–33°. After stirring for 30 min the precipitate triethylamine hydrochloride is removed by filtration and evaporation of the benzene affords a quantitative yield (7.05 g) of C-tribromomethyl-N-carbethoxyazomethine as a yellow oil, $\lambda_{max}^{CCl_4}$ (infrared), 1739 (C=O) and 1669 cm^{-1} (C=N). The compound decomposed on attempted vacuum distillation.

Addition of a sample of V to aqueous acetone and evaporation of the acetone affords ethyl 1-hydroxy-2,2,2-tribromoethylcarbamate, mp 137–138° (lit.[3] mp 132°).

Reaction of Ethyl 1-Hydroxy-2,2,2-trichloroethylcarbamate (**II**, **R** = C_2H_5) **with Phenyl Isocyanate.**—To a solution of 9.5 g (0.04 mol) of ethyl 1-hydroxy-2,2,2-trichloroethylcarbamate in 95 ml of benzene, containing 0.095 g of triethylenediamine (DABCO), 4.8 g (0.04 mol) of phenyl isocyanate is added and after refluxing for 100 min the solvent is evaporated to afford 12.2 g (86%) of **ethyl 1-phenylamino-2,2,2-trichloroethylcarbamate** (**VII**, **R** = C_2H_5, **R′** = C_6H_5), mp 87–88° after recrystallization from aqueous methanol.

The mixture melting point with a sample of VII (R = C_2H_5, R′ = C_6H_5) obtained from I (R = C_2H_5) and aniline was not depressed.

Reaction of Methyl 1-Hydroxy-2,2,2-trichloroethylcarbamate (**II**, **R** = CH_3) **with Isocyanates. A. Methyl Isocyanate.**—To a solution of 11.1 g (0.05 mol) of methyl 1-hydroxy-2,2,2-trichloroethylcarbamate in 110 ml of chlorobenzene 0.11 g (1% by weight) of potassium *t*-butoxide and 3.13 g (0.055 mol) of methyl isocyanate is added. The temperature rose to 32° and after short refluxing at 132° the solvent is evaporated under vacuum affording 10.75 g (88%) of **methyl 1-methylamino-2,2,2-trichloroethylcarbamate** (**VII**, **R** = CH_3, **R′** = CH_3): mp 109° after recrystallization from acetone; nmr ($CDCl_3$), singlet at 1.9 ppm (NH attached to CH_3 group), singlet at 2.57 ppm (N–CH_3), singlet at 3.75 ppm (O–CH_3), doublet at approximately 5.0 ppm (NH attached to the carbomethoxy group), and doublet at 5.8 ppm (CH group); intensity ratio, 1:3:3:1:1.

Anal. Calcd for $C_5H_9Cl_3N_2O_2$: C, 25.50; H, 3.85; N, 11.89. Found: C, 25.68; H, 3.94; N, 11.96.

B. Cyclohexyl Isocyanate.—The reaction is conducted analogously to A and a 76% yield of **methyl 1-cyclohexylamino-2,2,2-trichloroethylcarbamate** (**VII**, **R** = CH_3, **R′** = C_6H_{11}), mp 110–111° after recrystallization from ethyl acetate, is obtained.

Anal. Calcd for $C_{10}H_{17}Cl_3N_2O_2$: C, 39.55; H, 5.64; N, 9.22. Found: C, 39.73; H, 5.80; N, 9.15.

C. *p*-Toluenesulfonyl Isocyanate.—To a solution of 2.2 g (0.01 mol) of methyl 1-hydroxy-2,2,2-trichloroethylcarbamate in 25 ml of chloroform 1.97 g (0.01 mol) of *p*-toluenesulfonyl isocyanate is added. After refluxing for 30 min the solvent is evaporated and the residue is dissolved in glacial acetic acid. Addition of water causes precipitation of 2.15 g (51.5%) of **1-aminocarbethoxy-2,2,2-trichloroethyl *p*-toluenesulfonylcarbamate** (**X**, **R** = CH_3, **R′** = $CH_3C_6H_4$), mp 137–140°.

Anal. Calcd for $C_{12}H_{13}Cl_3N_2O_5S$: C, 34.34; H, 3.12; N, 6.67. Found: C, 34.14; H, 3.18; N, 6.41.

1,2,2,2-Tetrachloroethyl Isocyanate (**XI**). **A. From II, R** = C_2H_5.—To a solution of 18.8 g (0.08 mol) of II, R = C_2H_5, in chlorobenzene at reflux temperature simultaneously phosgene and a solution of 0.94 g of DMF in 25 ml of chlorobenzene are added over a period of 288 min. Distillation of the solvent and vacuum distillation of the residue affords 2.2 g (13.1%) of 1,2,2,2-tetrachloroethyl isocyanate, bp 41–45° (7.5 mm). Addition to excess methanol and evaporation affords methyl 1-methoxy-2,2,2-trichloroethylcarbamate, mp 64–65° (lit.[12] mp 64–65°).

B. From III, R = CH_3.—To a solution of 24.1 g (0.1 mol) of methyl 1,2,2,2-tetrachloroethylcarbamate in 100 ml of toluene carbonyl chloride and a solution of 2.4 g of DMF in 20 ml of toluene is added simultaneously at 110–115° over a period of 90 min. After removal of excess carbonyl chloride with nitrogen, evaporation of the solvent, and vacuum distillation of the residue, 10.05 g (48.2%) of 1,2,2,2-tetrachloroethyl isocyanate, bp 68–72° (20 mm), is obtained. Similarly a 40.2% yield of 1,2,2,2-tetrachloroethyl isocyanate can be obtained from III, R = C_2H_5.

The isocyanate is further characterized by conversion into 1-(diethylamino-2,2,2-trichloroethyl)-3-diethylurea, mp 51–52°, using 3 equiv of diethylamine.

Anal. Calcd for $C_{11}H_{22}Cl_3N_3O$: N, 13.17. Found: N, 13.12.

Diethyl 1-Isocyanato-2,2,2-trichloroethylphosphonate (**XII**).—To 104.5 g (0.5 mol) of 1,2,2,2-tetrachloroethyl isocyanate in 1000 ml of carbon tetrachloride 83 g (0.5 mol) of triethyl phosphite is added and the reaction mixture is refluxed for 105 min. Evaporation of the solvent affords 155 g of diethyl 1-isocyanato-2,2,2-trichloroethylphosphonate. A small sample was purified by vacuum distillation: bp 92–98° (0.2 mm); $\lambda_{max}^{CHCl_3}$ (infrared) 2475 (NCO) and 1266 cm^{-1} (P=O). The compound was further characterized by reaction with 1 equiv of aniline to afford **diethyl 1-phenylureido-2,2,2-trichloroethylphosphonate**, mp 202–204°.

Anal. Calcd for $C_{13}H_{18}Cl_3N_2O_4P$: B, 6.94. Found: N, 7.14.

Dimethyl 1-Aminocarbethoxy-2,2,2-trichloroethylphosphonate (**VIII**, **R** = C_2H_5, **R′** = CH_3). **A. From Dimethyl 1-Isocyanato-2,2,2-trichloroethylphosphonate.**—Addition of a sample of the isocyanate to excess ethanol, short refluxing in the presence of a catalytic amount of DABCO, and evaporation of the ethanol afford a quantitative yield of VIII (R = C_2H_5, R′ = CH_3): mp 88°; $\lambda_{max}^{CHCl_3}$ (infrared), 3425 (NH), 1730 (C=O), and 1266 cm^{-1} (P=O).

Anal. Calcd for $C_9H_{17}Cl_3NO_5P$: C, 25.59; H, 3.98; N, 4.26. Found: C, 25.42; H, 3.90; N, 4.43.

B. From Ethyl 1,2,2,2-Tetrachloroethylcarbamate (**II**, **R** = C_2H_5).—To 12.75 g (0.05 mol) of ethyl 1,2,2,2-tetrachloroethylcarbamate dissolved in 130 ml of carbon tetrachloride 6.2 g (0.05 mol) of trimethyl phosphite is added and the reaction mixture is refluxed for 2 hr. After evaporation of the solvent a quantitative crude yield (16.7 g) of VIII (R = C_2H_5, R′ = CH_3), is obtained, mp 83–88°. Recrystallization from benzene–ligroin raises the melting point to 88–89°.

C. From C-Trichloromethyl-N-carbethoxyazomethine (**I**, **R** = C_2H_5).—To 1.09 g (0.005 mol) of I, R = C_2H_5, in 15 ml of carbon tetrachloride 0.47 g (0.005 mol) of dimethylhydrogen phosphite and 4 drops of triethylamine are added and the reaction mixture is refluxed for 5 hr during which time the P–H absorption in the infrared spectrum at 2326 cm^{-1} disappears. Evaporation of the solvent and trituration with ligroin affords 1.3 g (83.5%) of VIII (R = C_2H_5, R′ = CH_3), mp 87–88°.

Registry No.—I, R = CH_3, 16723-29-8; I, R = C_2H_5, 16723-30-1; III, R = CH_3, 3659-10-7; ethyl 1-chloro-2,2,2-tribromoethylcarbamate, 16742-79-3; V, 16723-32-3; VII, R = C_2H_5, R′ = C_6H_5, 16723-33-4; VII, R = CH_3, R′ = CH_3, 1954-74-1; VII, R = CH_3, R′ = C_6H_{11}, 16723-35-6; VIII, R = R′ = C_2H_5, 16723-36-7; X, R = CH_3, R′ = 4-$CH_3C_6H_4$, 16723-37-8; XI, 15145-29-6; 1-(diethylamino-2,2,2-trichloroethyl)-3-diethylurea, 16723-39-0; XII, 16723-40-3; diethyl 1-phenylureido-2,2,2-trichlorodiethylphosphonate, 16723-41-4.

Acknowledgment.—We are indebted to Joseph Almaza for his assistance in the experimental aspects of this work.