(ϵ 119,860). PMR spectrum (CDCl₃ + CD₃OD), (δ , ppm): 3.05 and 3.25 [N(CH₃)₂], 4.2 ($\stackrel{\bigcirc}{CH}$), 5.76 (H^{β} and H^{δ}), 7.46 (H^{α}, H^{γ}, H^{ϵ}); $J_{\alpha,\beta} = J_{\beta,\gamma} = J_{\delta,\epsilon} = 12$ Hz.

Reaction of (I) (n = 2) with Methyl Nitroacetate. To 0.2 g of (I), n = 2, was added 0.1 g of $NO_2CH_2COOCH_3$ in 1 ml of dry ether, and the solid which separated was filtered off and washed with dry ether to gove 0.25 g of the salt (XVII), λ_{max} (C_2H_5OH) 412 nm (ϵ 102,000).

PMR spectrum (CDCl₃, δ , ppm): 3.0 and 3.25 [N(CH₃)₂], 3.5 (COOCH₃), 5.57 (H^β and H^δ), 6.45 (CH), 7.75 (H^α, H^γ, H^ε); $J_{\alpha,\beta} = J_{\beta,\gamma} = J_{\delta,\epsilon} = 12$ Hz.

CONCLUSIONS

1. A study has been made of the condensation of aminals and aminal-acetals of ω -dimethylaminopolyenals with ketones, β -diketones, and CH acids.

2. Several polyene ω -dimethylaminocarbonyl compounds (merocyanines) containing 3-5 double bonds have been synthesized.

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REACTIONS OF CCl₂CH₂CHCIR RADICALS GENERATED FROM 1,1,1,3-TETRACHLOROALKANES

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 CCl_2R' radicals are generated by the action of generating systems containing $Fe(CO)_5$ with various coinitiators on polychloroalkanes containing the CCl_3 group. The radicals are then reduced by hydrogen abstraction from a hydrogen donor (HD) and are competitively rearranged with hydrogen migration and dimerized. The reduction predominates when using isopropyl alcohol as the coinitiator [1], while the reduction reaction and rearrangement proceed with approximately identical rates when using HMPTA [2]. Thus, the yield of the products obtained from the rearranged radical $CCl_2CH_2CHClC_6H_{13}$ is 42%. In this case, rearrangements with presumed 1,7- and 1,8-hydrogen migrations are observed in addition to 1,5- and 1,6-hydrogen migrations. 1,1-Dichloroalkyl radicals obtained from 1,1,1-trichloroalkanes behave analogously in this system [3].

In the present work, we studied the reactions of radicals obtained from 1, 1, 1, 3-tetrachloroheptane (I) and 1, 1, 1, 3-tetrachlorooctane (VI) by the action of Fe(CO)₅ in the presence of HMPTA or triphenylphosphine at 140°C. The reaction of (I) yielded 1, 1, 3-trichloroheptane (II), 1, 1, 3, 5-tetrachloroheptane (III), 1, 1, 3, 6-tetrachloroheptane (IV), and 5, 7, 8, 10-tetrachloro-7-tetradecene (V) (Table 1). The formation of these compounds indicates that radicals (A) generated from (I) behave analogously to other $\dot{C}Cl_2R'$ radicals:

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TABLE 1. Reactions of Tetrachloroalkanes CCl_3CH_2CHClR Initiated by $Fe(CO)_5$ in Conjunction with HMPTA and Ph_3P at 140°C over 3 h in a Nitrogen Atmosphere*

R in tetra-	n of	Reaction products and their yield, %						
chloro-	ersio chloi les	reduction	luction rearrangement with hydrogen migration					
amane	Conv tetra a lkat		1,5	1,6	1,7	1,8	tion	
		_	Fe (CC)₅ + HMPTA			~~	
C ₄ H ₉ C ₅ H ₁₁ C ₆ H ₁₃ [2]	86 85 98	(II), 35 (VII), 39 (XII), 32	(III), 21 (VIII), 13 (XIII), 19	(IV), 19 (IX), 13 (XIV), 20	(X), 2 (XV), 2	 (XVI), 1,	(V), 5 (XI), 2 5 (XVII), 5	
			Fe (C	$(0)_{s} + Pb_{3}P$				
$C_4 H_9 C_5 H_{11} C_6 H_{13} \dagger$	75 78 80	(11), 6 (VII), 9 (XII), 7	(III), 18 (VIII), 17 (XIII), 16	(IV), 16 (IX), 17 (XIV), 18	(X), 2 (XV), 2	(XVI), 2	(V), 15 (XI), 13 (XVII), 14	

* 20 mole % $Fe(CO)_5$, 40 mole % HMPTA or Ph_3P relative to the tetrachloroalkane.

† Authentic samples for identification of (XII)-(XVII) were obtained in our previous work [2].



Similar products in the reaction of 1, 1, 1, 3-tetrachlorooctane (VI), namely, 1, 1, 3-trichlorooctane (VII), 1, 1, 3, 5-tetrachlorooctane (VIII), 1, 1, 3, 6-tetrachlorooctane (IX), 1, 1, 3, 7-tetrachlorooctane (X), and 6, 8, 9, 11-tetrachloro-8-hexadecene (XI), are formed as the result of reduction rearrangements with 1, 5-, 1, 6-, and a presumed 1, 7-hydrogen migration, and dimerization of $\dot{CCl}_2CH_2CHClC_5H_{11}$ radicals (B) (see Table 1).

The results indicate that, as in the case of 1, 1, 1, 3-tetrachlorononane [2], the action of the Fe(CO)₅⁺ HMPTA system on tetrachloroalkanes (I) and (VI) gives competing reduction and rearrangement with hydrogen migration in the radicals formed (A) and (B) which proceed with about the same rate, judging from the yields of the corresponding products. The products formed due to 1, 5- and 1, 6-hydrogen migration predominate in the rearrangement products. A compound which likely forms due to the rearrangement of radical (B) with a 1, 7-hydrogen migration is obtained in low yield.

The use of Ph_3P as the coinitiator for $Fe(CO)_5$ holds interest in light of its low hydrogen donor capacity. As a consequence, we may presume that the ratio of the yields of the products of the competing reduction, rearrangement, and dimerization reactions will be different than upon the action of $Fe(CO)_5$ +HMPTA on 1,1,1,3tetrachloroalkanes. This hypothesis was checked for reactions initiated by the $Fe(CO)_5$ +PPh₃ system. Indeed, Table 1 shows that the yield of the reduced products is markedly reduced (down to 6-9%), while the composition and yield of the rearranged products is hardly changed. The yield of the dimerization products is increased by 9-11%.

The structure of these products was confirmed by 13 C NMR spectroscopy (Table 2). The assignment of the 13 C NMR signals was carried out by calculation of the 13 C NMR shifts by an additive scheme taking increments into account [4]. The spectra of n-heptane and n-octane were taken as the bases.

The spectra of tetrachloroalkanes (I) and (VI) contain characteristic signals for the CCl_3CH_2CHCl fragment attached to an alkyl group and differ from the spectra of trichloroalkanes (II) and (VII) only in the signals for C^1-C^3 , which indicates the loss of one chlorine atom from the CCl_3 group.

The spectra of products (III), (IV), (VIII), (IX), and (X), which are isomeric to tetrachloroalkanes (I) and (VI), lack CCl_3 group signals in the vicinity of 97 ppm and have signals for the $CHCl_2CH_2CHCl$ fragment

		1	1	13C NIMP che	mical shifts	Å nom from	T MS (found/	calculated	-
-						, have not did to			
Compound	Chemical formula	ū	บ	ບ	Ċ	ů	ů	ŭ	G
(1)	$\begin{bmatrix}1&2&3&4&5&6&7\\ccl_{3}cH_{2}cHclcH_{2}cH_{2}cH_{2}cH_{3}cH_{3}\end{bmatrix}$	6'96	62,4	57,2	38,6	28,0	22,0	13,9	
(11)	CHCl ₂ CH ₂ CHClCH ₂ CH ₂ CH ₂ CH ₃ CH ₈	95,0 70,4 68,3	61,2 51,7 50,9	57,3 58,6 58,6	37,8 37,8 37,8	28,9 28,9	22,6 22,6 22,6	13,7 13,7	
* (III)	CHCl2CH2CHCICH2CHCICH2CH3	69,9 68,3	51,7 50,9	56,5 55,5	$\frac{46,3}{45,6}$	60,8 59,8 62,4	31,6 31,4	$\frac{10.9}{10.6}$	
(II)	CHCl ₂ CH ₂ CHClCH ₂ CH ₂ CHClCH ₅	70,3 68,3	51,5 50,9	58,2 58,7 58,6	35,2 34,7 34,7	36,2 36,9 37,7	51,3 56,8 57,6	25,3 25,4	
(IV)	1 2 3 4 5 6 7 8 CCI ₃ CH ₂ CHCICH ₂ CH ₂ CH ₂ CH ₃ CH ₃	<u>96,5</u>	62,3	57,0 52,0	38,5	25,2 96 3	30,6	22,0	13,5 13,6
(111)	CHCl ² CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃ CH ₃	94,9 70,6 68,2	51,0 51,0	59,1 58,7	37,9 38,2	25,7 26,3	31.1 32.0	22,4	13,9 13,6
(IIII)	CHCl ₂ CH ₂ CHClCH ₂ CHClCH ₂ CH ₂ CH ₃ CH ₃	$\frac{70,2}{68,2}$	51,6 51,0	56,7 55,7 55,6	$\frac{46,5}{46,0}$	59,9 59,9	40,5 40,8 6,5	19,4 19,6 19,6	13,4
(XI)	GHGI2GH2CHCICH2CH2CHCICH2CH3	70,4	51.5	58,4 58,4	34,6	34, 1 35.1	64,5 64,2	31,4 31.5	10,8
(X) †	CHCl2CH2CHCICH2CH2CH2CH2CH3	70,4 68,2	51,5	59,0 58,7	37,3 38,2	23,3	39,4 40,9	57,9 57,7	25,2
* 40.9 7		turo a cum	notrio oor	itare in (II		(TTT) and	TV) the	require	Jf.

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TABLE 2. ¹³C NMR Spectra Data for Tri- and Tetrachloroalkanes

• As a consequence of the presence of two asymmetric centers in (III), (IV), (VIII), and (IX), the number of signals for each carbon atom in the spectra of these compounds may be doubled. • From a spectrum of a mixture of 30% (IX) + 70% (X).

and a second CHCl group which occupies a different position in these compounds. Thus, the chlorine atom in (III) is at C⁵ as indicated by the upfield shift of C³ (CHCl) and C⁷ (CH₃) due to the γ -effect of the chlorine atom at C⁵, while the chemical shifts of C⁴ and C⁶ indicate the presence of two and one β -chlorine atoms, respectively.

This CHCl group in (IV) is at C⁶ as indicated by the chemical shifts of C⁵ (CH₂) and C⁷ (CH₃) which are enhanced by the chlorine β -effect. In the isomeric tetrachlorooctanes (VIII) and (IX), the second CHCl group is at C⁵, and C⁶, respectively, and these products have their own characteristic spectra. Thus, for example, in (VIII) the signals for C³ (CHCl) and C⁷ (CH₂) are shifted upfield due to the γ -effect of the chlorine atom at C⁵.

The signals for the CH_2CH_3 fragment in (IX) coincide with those for the same fragment in (III).

The spectrum of (X) is in accord with the assumption that the second CHCl group is at C⁷. This is indicated by the chemical shifts for C⁶ (CH₂) and C⁸ (CH₃), which are enhanced due to the presence of a chlorine atom in the β -position, as in (IV). In addition, the signals for the CHClCH₃ fragment in the spectrum of (X) coincide with the corresponding signals in the spectrum of (IV).

EXPERIMENTAL

The gas-liquid chromatographic (GLC) analysis was carried out on an LKhM-8MD5 chromatograph with a katharometer and temperature programming from 140° to 270°C on the columns: 1) 1 m \times 3 mm packed with 20% SKTFT-50 on Chromatone N-AW (0.16-0.20 mm) and 2) 1 m \times 3 mm packed with 15% Carbowax 20M on Chromatone N-AW-HMDS (0.16-0.20 mm). The product yields were found using an internal standard: 1, 1, 1, 3tetrachlorooctane (VI) was used for experiments with 1, 1, 1, 3-tetrachloroheptane (I), and (I) was used for experiments with (VI) and 1, 1, 1, 3-tetrachlorononane. Preparative GLC was carried out on a Tsvet-4-67 chromatograph with a katharometer on a 1-m \times 9-mm column packed with 20% SKTFT-50 on Chromatone N-AW (0.20-0.25 mm).

The ¹³C NMR spectra were obtained for 20-80% solutions in CCl_4 using a Bruker HX-270 Fourier spectrometer at 67.88 MHz.

<u>1,1,1,3-Tetrachloroheptane</u> (I) was obtained from 250 mmoles 1-hexene, 500 mmoles CCl_4 , 25 mmoles $Fe(CO)_5$, 100 mmoles HMPTA, and 12.5 mmoles N,N-dichloro-p-chlorobenzenesulfamide according to our previous procedure [5] in 80% yield, bp 63°C (1 mm), n_D^{20} 1.4740, d_4^{20} 1.2519 [6].

1,1,1,3-Tetrachlorooctane (VI) [7, 8] was obtained analogously to (I) in 75% yield.

Reactions of 1, 1, 1, 3-Tetrachloroheptane (I) and 1, 1, 1, 3-Tetrachlorooctane (VI) Initiated by the $Fe(CO)_5$ + HMPTA System. All the experiments indicated in Table 1 and preparative runs for isolating the individual products were carried out by a general method [2]. For the preparative runs, reaction mixtures contained 100 mmoles (I) or (VI), 20 mmoles $Fe(CO)_5$, and 40 mmoles HMPTA, treated as in our previous work [2], and subjected to fractional distillation in vacuum.

1,1,3-Trichloroheptane (II) was isolated upon repeated distillation of the fraction with bp 70-72°C (8 mm), bp 74°C (8 mm), n_D^{20} 1.4632, d_4^{20} 1.1653. Found: C, 41.07; H, 6.27; Cl, 52.90%. Calculated for $C_7H_{13}Cl_3$: C, 41.28; H, 6.39; Cl, 52.33%.

1,1,3,5-Tetrachloroheptane (III) was isolated from the fraction with bp 73-75°C (1 mm) by preparative GLC, n_D^{20} 1.4839, d_4^{20} 1.2864. Found: C, 35.77; H, 5.04; Cl, 59.54%. Calculated for $C_7H_{12}Cl_4$: C, 35.29; H, 5.04; Cl 59.66%.

1,1,3,6-Tetrachloroheptane (IV) was isolated from the fraction with bp 76-77°C (1 mm) by preparative GLC, n_D^{20} 1.4852, d_4^{20} 1.2836. Found: C, 35.88; H, 4.97; Cl, 59.64%. Calculated for $C_7H_{12}Cl_4$: C, 35.29; H, 5.04; Cl, 59.66%.

5,7,8,10-Tetrachloro-7-tetradecene (V) was obtained by repeated distillation from the fraction with bp 160-165°C (1 mm), bp 167°C (1 mm). Found: C, 50.43; H, 7.22; Cl, 42.14%, mol.wt. 334 (M⁺). Calculated for $C_{14}H_{24}Cl_4$: C, 50.30; H, 7.19; Cl, 42.51%, mol. wt. 334. ¹³C NMR spectrum (δ , ppm): 13.8 (C^{1,14}), 22.0 (C^{2,13}), 28.3 (C^{3,12}), 36.8 (C^{4,11}), 58.6 and 58.4 (C^{5,10}), 44.4 and 44.2 (C^{6,9}), 128.7 (C^{7,8}).

1,1,3-Trichlorooctane (VII) [7, 8] was obtained by repeated distillation from the fraction with bp $63-67^{\circ}C$ (1 mm).

Preparative GLC of the fraction with bp 67-68°C (1 mm) gave 1, 1, 3, 5-tetrachlorooctane (VIII) and 1, 1, 3, 6-tetrachlorooctane (IX). For (VIII): n_D^{20} 1.4831; d_4^{20} 1.2401. Found: C, 38.13; H, 5.42; Cl, 56.46%.

Calculated for C₈H₁₄Cl₄: C, 38.10; H, 5.56; Cl, 56.35%.

For (IX): n_D^{20} 1.4878, d_4^{20} 1.2300. Found: C, 38.05; H, 5.38; Cl, 56.59%. Calculated for $C_8H_{14}Cl_4$: C, 38.10; H, 5.56; Cl, 56.35%.

A 3:7 mixture of 1,1,3,6-tetrachlorooctane (IX) and 1,1,3,7-tetrachlorooctane (X) was obtained by preparative GLC from the fraction with bp 76-84°C (1 mm). Found: C, 38.15; H, 5.49; Cl, 56.57%. Calculated for $C_8H_{14}Cl_4$: C, 38.10; H 5.56; Cl, 56.35%.

Repeated distillation of the fraction with bp 165-168°C (1 mm) gave 6,8,9,11-tetrachloro-8-hexadecene with bp 172°C (1 mm). Found: C, 53.24; H, 7.78; Cl, 39.00%, mol. wt. 362 (M⁺). Calculated for $C_{16}H_{28}Cl_4$: C, 53.04; H, 7.73; Cl, 39.23%, mol. mass 362. ¹³C NMR spectrum (δ , ppm): 13.9 (C^{1,16}), 22.4 (C^{2,15}), 31.1 (C^{3,14}), 25.8 (C^{4,13}), 37.1 (C^{5,12}), 58.7 and 58.4 (C^{6,11}), 44.4 and 44.2 (C^{7,10}), 128.6 (C^{8,9}).

Reactions of (I), (VI), and 1,1,1,3-Tetrachlorononane Initiated by the $Fe(CO)_5 + Ph_3P$ System. A mixture of 12.5 mmole (I), (VI), or 1,1,1,3-tetrachlorononane, 2.5 mmole $Fe(CO)_5$, and 5 mmoles Ph_3P was heated with stirring in a nitrogen stream for 3 h at 140°C. The reaction mixture was treated as in the experiments with HM-PTA [2]. The reaction products were identified and their yields determined by GLC using authentic samples (see Table 1).

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CONCLUSIONS

1. The reduction of 1, 1, 1, 3-tetrachloroheptane and 1, 1, 1, 3-tetrachlorooctane to the corresponding 1, 1, 3-trichloroalkanes and the rearrangement of 1, 1, 1, 3-tetrachloroheptane to 1, 1, 3, 5- and 1, 1, 3, 6-tetra-chloroheptanes and of 1, 1, 1, 3-tetrachlorooctane to 1, 1, 3, 5-, 1, 1, 3, 6-, and 1, 1, 3, 7-tetrachlorooctanes initiated by the Fe(CO)₅ + HMPTA system proceed at 140°C with comparable rates.

2. The action of $Fe(CO)_5$ together with triphenylphosphine on 1, 1, 1, 3-tetrachloroalkanes gives only a slight amount of reactions of these compounds, while the rearrangement products predominate.

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