Derivatives of 5-Bromo-1,1,1-trichloro-3-pentene

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5-Bromo-1,1,1-trichloro-3-pentene (I) has been synthesized from butadiene and bromotrichloromethane. Various addition reactions to the double bond and metathetical reactions of I, as well as the reactions of the resultant products, are described. The preparation of the acetate, its conversion to the alcohol, and finally the preparation of the chloroformate are described. Several derivatives of both the alcohol and the chloroformate are also given.

5 - Bromo - 1,1,1 - trichloro - 3 - pentene (I) was first prepared by Kharasch[1-3] and his associates by the reaction of 1,3-butadiene and bromotrichloromethane. They also isolated the 1,2-addition product 3 - bromo - 5,5,5 - trichloro - 1 - pentene. Joyce[4] describes several reactions of 1,1,1,5-tetrachloro-3-pentene. No extensive study of 5-bromo-1,1,1-trichloro-3-pentene has been undertaken. I has been prepared in 76% yield by the reaction of butadiene with excess bromotrichloromethane, using both peroxide and ultraviolet light as initiators. None of the 1,2-isomer was isolated. This might be due either to the experimental conditions or to an allylic rearrangement which has taken place to give one isomer. A small amount of a higher boiling liquid, believed to be of polymeric nature but not identified, was also isolated.

The bromination and chlorination of the double bond of I and its various derivatives in carbon tetrachloride yielded the expected compounds in 42–87% yields (see Table I).

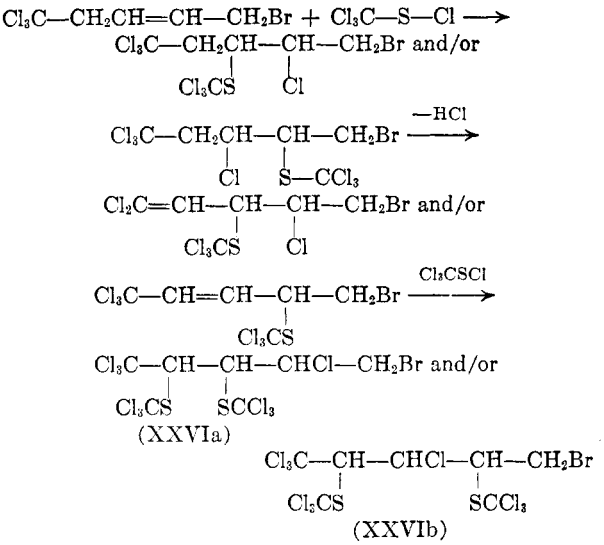
The various metathetical reactions of I were carried out in aqueous ethyl alcohol; the products were isolated in yields varying from 36–88% (see Table II).

The reaction of I with sodium sulfide produced the thioether X. The hydrogen peroxide oxidation of X in acetic acid gave the sulfone XII.

The condensation of I with ethyl malonate and ethyl acetoacetate gave XVIII and XX. The acid hydrolysis of XVIII yielded the trichloroheptenoic acid XIX. The alkaline cleavage of XX produced the ketone XXI in 73% yield. The pyrazolinones XXII and XXIII were produced from the reaction of XX with phenylhydrazine and *p*-nitrophenylhydrazine.

From I and carbon disulfide in aqueous diethylamine the trichloropentenyl diethyldithiocarbamate XXV was isolated.

The addition of perchloromethyl mercaptan to the double bond of I did not give the expected bromotetrachloro (trichloromethylthio) pentane.[5] The elemental analysis of the isolated product was consistent with a bromotetrachlorobis(trichloromethylthio)pentane (XXVIa and b) structure. The isolation of such a material may be explained by the following sequence of reactions:



The first addition product is thermally unstable and splits out hydrogen chloride, giving a bromotrichloro(trichloromethylthio)pentene, which adds another mole of perchloromethyl mercaptan to give XXVIa or XXVIb. This mechanism is consistent with observations[6] regarding the formation of 1,1-dichloro-1-nonene from 1,1,1-trichlorononane. Similar results were obtained with perchloromethyl mercaptan when the acetate V was substituted for I. The product isolated was a tetrachlorobis (trichloromethylthio) pentyl acetate (XXVII).

The transesterification of the acetate VI gave the corresponding alcohol XXXI.

While attempting to prepare 5,5,5,-trichloro-2-pentenyl tetrahydro-1, 1-dioxo-3-thienyl ether from XXXI and butadiene sulfone, bis(5,5,5,-trichloro-2-pentenyl) ether (XXXII) was isolated. The formation of the symmetrical ether may have been due to the decomposition of the butadiene sulfone to sulfur dioxide and butadiene.

(1) M. S. Kharasch, O. Reinmuth, and W. H. Urry, *J. Am. Chem. Soc.*, **69**, 1105 (1947).

(2) M. S. Kharasch and M. Sage, *J. Org. Chem.*, **14**, 537 (1949).

(3) M. S. Kharasch, E. Simon, and W. Nudenberg, *ibid.*, **18**, 328 (1953).

(4) R. M Joyce, Jr., U.S. Patent 2,425,426 (August 12, 1947).

(5) D. E. Badertscher, H. G. Berger, and F. M. Seger, U.S. Patent 2,319,183 (May 11, 1943).

(6) R. M. Joyce, Jr., U.S. Patent 2,410,541 (November 5, 1946).

TABLE I

DERIVATIVES OF 5-BROMO-1,1,1-TRICHLORO-3-PENTENE

$$Cl_3—CH_2—\underset{\displaystyle Y}{CH}—\underset{\displaystyle Y}{CH}—CH_2—Z$$

	Z	Y	Moles of halogen Y	B.p. °C./mm.	Refractive index $n^{20}D$	Yield, %	Formula	Calcd. C	Calcd. H	Found C	Found H
II	Br	Br	0.175	96–99/0.03	1.5803	77	$C_5H_6Br_3Cl_3$	14.50	1.47	15.17	1.50
III	Br	Cl	.157	121–124/2.5	1.5402	88	$C_5H_6BrCl_5$	18.60	1.86	19.10	1.89
V	CN	Cl	.366	119–120/0.5	1.5200	55	$C_6H_6Cl_5N$	26.78	2.13	26.73	2.13
VII	$OCCH_3$	Cl	.238	88–91/0.5	1.4996	42	$C_7H_9Cl_5O_2$	27.80	2.98	27.99	3.10

The ether XXVIII and the esters XXIX, XXX, XXXIII to XXXV were prepared in 43–94% yields by the reaction of I with phenol or the appropriate acid together with potassium carbonate in ethyl methyl ketone. A second procedure used was to allow the alcohol XXXI and the corresponding acid chloride to react (see Table III).

The trichloropentenyl carbonate XL was isolated from the reaction of XXXI and ethyl chloroformate. The phosgenation of XXXI yielded the chloroformate XLI in 93% yield.

The carbamates were prepared in 32–92% yields from the reaction of the alcohol XXXI and the appropriate isocyanate, or the reaction of the amine and the chloroformate XLI (see Table IV).

Ammonium O,O-diethyl phosphorodithioate and the chloroformate XLI gave the ester XLIX in 76% yield. Urea and XLI gave the allophanate L in 44% yield.

The infrared spectra of I, IV, VIII, and XXXI showed no terminal double bonds. The standard reference compounds were 1-chloro-5-methoxy-2-pentene and 3-chloro-5-methoxy-1-pentene prepared by the reaction of monochloromethyl ether and butadiene.[7]

The purpose of this research was to find novel, useful pesticides. The results of the biological screening of these compounds may be reported at a later date.

Experimental

5-Bromo-1,1,1-trichloro-3-pentene (I).—Butadiene (1.73 moles) was bubbled into a solution of 313 g. (1.57 moles) of bromotrichloromethane and 7 g. of 25% acetyl peroxide in dimethyl phthalate. The mixture was heated with an ultraviolet light which acted as an initiator for the free radical addition. Over an 8-hr. period the temperature rose from 50° to a maximum of 110°. Bromotrichloromethane was removed by distillation at reduced pressure. The main fraction, 296 g. (75%), distilled at 75–76° (1 mm.), $n^{20}D$ 1.5346.

Anal. Calcd. for $C_5H_6BrCl_3$: C, 23.60; H, 2.37. Found: C, 23.71; H, 2.36.

The infrared spectrum showed no evidence of a terminal double bond, thus indicating no 1,2-addition product. A higher boiling fraction with polymeric characteristics was also isolated.

3,4,5-Tribromo-1,1,1-trichloropentane (II), 5-bromo-1,1,1,3,4-pentachloropentane (III), 3,4,6,6,6-pentachlorohexane nitrile (V), and 2,3,5,5,5-pentachloropentyl acetate (VII) were prepared by the general method outlined (see Table I).

The trichloro-2-pentenyl derivatives (0.15 mole) were dissolved in 250 ml. of carbon tetrachloride. Into this solution was bubbled 12.2 g. (0.172 mole) of chlorine gas. After the exothermic reaction had subsided, the reaction mixture was stirred for an additional hour. The carbon tetrachloride was distilled at reduced pressure and the residual oil vacuum distilled.

6,6,6-Trichlorohexene-3-nitrile (IV), 5,5,5-trichloro-2-pentenyl acetate (VI), N-(5,5,5-trichloro-2-pentenyl)phthalimide (IX), 5,5,5-trichloro-2-pentenyl-1-thiol (XI), 5,5,5-trichloro-2-pentenyl thiouronium bromide (XIII), 5,5,5-trichloro-2-pentenyl hexaminium bromide (XIV), 5,5,5-trichloro-1-iodo-2-pentene (XV), O,O-diethyl S-(5,5,5-trichloro-2-pentenyl)phosphorodithioate (XVI), 5,5,5-trichloro-2-pentenyl ethyl xanthate (XVII), and 5,5,5-trichloro-2-pentenyl N-(1-methylpropyl)-N-(tetrahydro-1,1-dioxo-3-thienyl)dithiocarbamate (XXIV) were prepared by the general method outlined for the preparation of 5,5,5-trichloro-2-pentenyl thiocyanate (VIII) (see Table II).

Sodium thiocyanate, 35 g. (0.43 mole), was refluxed for 5 hr., with 100 g. (0.396 mole) of I in 160 ml. of 60% aqueous ethyl alcohol; the mixture was cooled, poured into water, and the organic layer separated. The aqueous layer was extracted with chloroform, combined with the organic layer and dried over magnesium sulfate. The chloroform was distilled at reduced pressure and the product vacuum distilled. The main fraction, 77 g. (84%), distilled at 88° (0.07 mm.), $n^{20}D$ 1.5447.

Anal. Calcd. for $C_9H_9Cl_3NS$: C, 31.20; H, 2.58. Found: C, 31.07; H, 2.48.

The infrared spectrum showed no terminal double bond, thus eliminating the possibility of an allylic rearrangement. The compound gave a sharp peak at 4.65 μ, indicating it was the thiocyanate and not the isothiocyanate. Standard reference compounds were allyl isothiocyanate and 5-methoxy-2-pentenyl isothiocyanate.[8]

Bis(5,5,5-trichloro-2-pentenyl) Sulfide (X).—Sodium sulfide monohydrate, 50 g. (2.21 moles), was treated with 100 g. (0.390 mole) of I in 150 ml. of 70% aqueous ethyl alcohol. After the initial exothermic reaction had subsided, the solution was refluxed for 4 hr. After cooling overnight, the solution was poured into water and the organic layer separated. The aqueous layer was extracted with ether and the combined organic layers dried over magnesium sulfate and filtered. The ether was distilled, leaving 61.5 g. of an oil, which upon cooling gave 22 g. (29.5%) of a solid melting at 54.5° when recrystallized from petroleum ether.

Anal. Calcd. for $C_{10}H_{12}Cl_6S$: C, 31.9; H, 3.19. Found: C, 31.84; H, 3.19.

The remaining oil from the filtrate was vacuum distilled. After a small amount of material, believed to be the thioalcohol, distilled at 58–62° (0.1 mm.); the material decomposed.

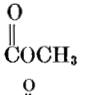
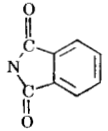
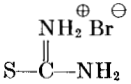
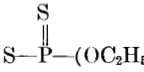
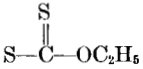
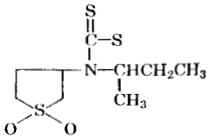
(7) L. H. Amundsen and W. F. Brill, *J. Am. Chem. Soc.*, **73**, 1834 (1951).

(8) W. S. Emerson, G. F. Deebel, and R. I. Longley, Jr., *J. Org. Chem.*, **14**, 696 (1949).

TABLE II

DERIVATIVES OF 5-BROMO-1,1,1-TRICHLORO-3-PENTENE

$Cl_3C—CH_2CH=CH—CH_2—Z$

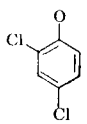
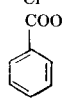
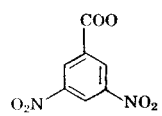
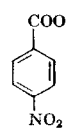
	Z	Reagent to produce Z	Reaction solvent	Moles of reagent	M.p., °C.[a]	B.p., °C./mm.	Refractive index at 20°	Yield, %	Formula	Calcd. C	Calcd. H	Found C	Found H
IV	CN	Potassium cyanide	Aqueous ethyl alcohol 75%	0.276		112–114/1.5	1.5014	58	$C_6H_6Cl_3N$	36.1	3.02	35.4	3.02
VI		Potassium acetate	Acetic acid	.49		78–80/0.5	1.4878	83	$C_7H_9Cl_3O_2$	36.20	3.88	36.46	3.77
IX		Potassium phthalimide	Dimethyl formamide	.15	83–84			36	$C_{13}H_{10}Cl_3NO_2$	49.20	3.16	49.17	3.08
XI	SH	Sodium hydrosulfide	Aqueous ethyl alcohol 80%	.278		60–61/0.1	1.514	53	$C_5H_7Cl_3S$	29.2	3.40	29.75	3.27
XIII		Thiourea	Aqueous ethyl alcohol 85%	.355	166–167		...	85	$C_6H_{10}BrCl_3N_2S$	22.0	3.05	22.02	2.96
XIV	$N_4^{\oplus}(CH_2)_6Br^{\ominus}$	Hexamethylenetetramine	Chloroform	.355	179		...	100	$C_{11}H_{18}BrCl_3N_4$	33.50	4.57	33.53	4.64
XV	I	Sodium iodide	Acetone	.240		86–90/0.8	1.5780	60.5	$C_5H_6Cl_3I$	20.00	2.00	20.82	2.07
XVI		Ammonium *o,o*-diethyl phosphorodithioate	Aqueous ethyl alcohol 70%	.20	...	...	...	71	$C_9H_{16}Cl_3O_2PS_2$	30.20	4.50	30.85	4.76
XVII		Sodium ethyl xanthate	Ethyl alcohol	.44		149–153/1.2	1.5681	53	$C_8H_{11}Cl_3OS_2$	32.60	3.75	32.56	3.91
XXIV		Sodium *N*-methylpropyl 1,1-dioxotetrahydro-3-thienyl dithiocarbamate	Aqueous ethyl alcohol 45%	.245	103–104		...	88	$C_{11}H_{22}Cl_3NO_2S_3$	38.40	4.80	38.39	4.93

[a] Recrystallized from ethyl alcohol. [b] The material decomposed when an attempt was made to distil the product under vacuum.

TABLE III

5,5,5-TRICHLORO-2-PENTENYL ETHER OR ESTER

$Cl_3C—CH_2CH=CH—CH_2—R$

	R	Acidic reagent	Moles	M.p., °C.[a]	B.p., °C./mm.	Refractive index $n^{20}D$	Yield %	Formula	Calcd. C	Calcd. H	Found C	Found H
XXVIII		2,4-Dichlorophenol	0.214		173-177/1.6	1.5747	65	$C_{11}H_9Cl_5O$	39.50	2.68	39.59	2.56
XXIX		Benzoic acid	.245		156-158/3.	1.5445	43	$C_{12}H_{11}Cl_3O_2$	49.00	3.74	49.13	3.96
XXX	C_3H_7COO	Butyric acid	.50		110-111/1.	1.4837	86	$C_9H_{13}Cl_3O_2$	41.64	5.04	41.42	4.94
XXXIII	Cl_3CCOO	Trichloroacetyl chloride	.194		116-117/0.7	1.5146	94	$C_7H_6Cl_6O_2$	25.00	1.79	24.31	1.81
XXXIV		*p*-Nitrobenzoyl chloride	.135	82-83	...	...	64	$C_{12}H_{10}Cl_3NO_4$	42.70	2.95	42.70	2.90
XXXV		3,5-Dinitrobenzoyl chloride	.109	68-70	...	...	49.5	$C_{12}H_9Cl_3N_2O_6$	37.87	2.37	37.79	2.46

[a] Recrystallized from ethanol.

TABLE IV

O-(5,5,5-TRICHLORO-2-PENTENYL) CARBAMATE

$Cl_3C—CH_2CH{=}CH—CH_2—O—C(=O)—N(R)R'$

	R	R'	Iso-cyanate or amine	Moles	M.p., C°.	B.p., °C./mm. —	Refractive index $n^{20}D$	Yield %	Formula	Calcd. C	Calcd. H	Found C	Found H
XLII	H	H	NH_3	Excess	94–96[a]	. . .	. . .	32	$C_6H_8Cl_3NO_2$	31.00	3.44	30.48	3.50
XXXVI	H	C_4H_9	C_4H_9NCO	0.504	. . .	148–151/0.3	1.4930	43	$C_{10}H_{16}Cl_3NO_2$	41.70	5.50	42.32	6.01
XXXVII	H	C_3H_7	C_3H_7NCO	.282		125–126/0.1	1.4940	59	$C_9H_{14}Cl_3NO_2$	39.40	5.10	38.56	5.03
XLV	C_2H_5	C_2H_5	$(C_2H_5)_2NH$	.48		110–112/0.1	1.4920	80	$C_{10}H_{16}Cl_3NO_2$	41.70	5.55	41.2	5.46
XLIV	CH_3	CH_3	$(CH_3)_2NH$	Excess		120–123/0.1	1.4962	68	$C_6H_{12}Cl_3NO_2$	36.92	4.60	37.15	4.44
XLIII	H	CH_3	CH_3NH_2	Excess		116–117/0.4	1.5048	68	$C_7H_{10}Cl_3NO_2$	34.00	4.03	34.42	4.10
XXXVIII	H	CHC_2H_5 (—CH_3)	CH_3—$CHNCO$—C_2H_5	0.504		134/0.5	1.4878	43	$C_{10}H_{16}Cl_3NO_2$	41.70	5.50	41.71	5.53
XXXIX	H	C_6H_5	C_6H_5NCO	.150	56 7[a]		. . .	49	$C_{12}H_{12}Cl_3NO_2$	46.80	3.90	47.14	4.05
XLVI	H	C_6H_4Cl	2-Cl aniline	.20		. . .	1.5601	45	$C_{12}H_{11}Cl_4NO_2$	42.11	3.22	42.01	3.51
XLVII	H	$C_6H_3Cl_2$	2,4-Cl_2 aniline	.2		. . .	1.5743	92	$C_{12}H_{10}Cl_5NO_2$	38.20	2.34	38.23	2.34
XLVIII	H	$C_6H_2Cl_3$	2,4,6-Cl_3 aniline	.199	93[b]	. . .		52	$C_{12}H_9Cl_6NO_2$	35.00	2.18	35.65	2.10

[a] Recrystallized from ethyl alcohol. [b] Recrystallized from n-hexane.

Bis(5,5,5-trichloro-2-pentenyl) Sulfone (XII).—Bis(5,5,5-trichloro-2-pentenyl) sulfide, 37.7 g. (0.1 mole), was dissolved in 150 ml. of hot acetic acid. To this solution was added 23 g. of 30% hydrogen peroxide (6.9 g., 0.2 mole). After all the peroxide had been added the solution was heated at 100° for 2 hr. The solution, upon cooling, deposited crystals of the sulfone. The solid was filtered and 30 g. (74%) of the crude material was isolated. The crude sulfone was recrystallized from ethanol, and 26 g. (64%) of product melting at 97–98°, was isolated.

Anal. Calcd. for $C_{10}H_{12}Cl_6O_2S$: C, 29.50; H, 2.95. Found: C, 29.35; H, 3.00.

Diethyl 5,5,5-Trichloro-2-pentenylmalonate (XVIII).—To a solution of 12 g. (0.521 g.-atom) of metallic sodium in 200 ml. of absolute ethyl alcohol, 160 g. of ethyl malonate (1 mole) was added dropwise. After the malonate had been added, 126 g. (0.5 mole) of I was added dropwise. The solution was then refluxed for 1 hr. The ethyl alcohol was distilled at reduced pressure and the residue washed with water. The organic layer was separated, dried, and vacuum distilled. After the unchanged ethyl malonate was distilled there was isolated 27 g. (16.5%) of a material distilling at 144–148° (0.8 mm.), $n^{20}D$ 1.4755.

Anal. Calcd. for $C_{12}H_{17}Cl_3O_4$: C, 43.40; H, 5.10. Found: C, 42.71; H, 5.17.

7,7,7-Trichloro-4-heptenoic Acid (XIX).—XVIII, 43 g. (0.13 mole), was dissolved in a mixture of 80 ml. of acetic acid and 50 ml. of hydrochloric acid and refluxed for 10 hr. The organic layer was separated from the aqueous layer and the latter extracted with chloroform. The chloroform solution was mixed with the crude acid and the chloroform distilled. The residual oil was heated at 170–180° until no more carbon dioxide gas evolved. The residue was taken up in 50 ml. of 10% sodium hydroxide; the aqueous solution was extracted with ether to remove any unchanged malonate. The aqueous layer was acidified with hydrochloric acid and the organic acid separated. The acid was vacuum distilled and the main fraction, 20 g. (67%) distilled at 142–144° (1.8 mm.), $n^{20}D$ 1.5008.

Anal. Calcd. for $C_7H_9Cl_3O_2$: C, 36.40; H, 3.88. Found: C, 37.01; H, 3.88.

Ethyl 2-Acetyl-7,7,7-trichloro-4-heptenoate (XX).—Metallic sodium, 13.8 g. (0.6 g.-atom) was dissolved in 140 g. of absolute ethyl alcohol. After all the sodium had been dissolved, 80 g. (0.615 mole) of ethyl acetoacetate was added. To this solution was added 151.2 g. (0.6 mole) of I dropwise. The solution was then refluxed for 10 hr. The ethyl alcohol was distilled and the residue taken up in water. The crude ester was separated from the aqueous solution and the latter extracted with chloroform. The crude ester and chloroform solution was mixed and dried over magnesium sulfate. The solution was filtered and the chloroform distilled at reduced pressure. The residual product was vacuum distilled, the main fraction, 112.7 g. (62%), distilling at 128–132° (0.5 mm.), $n^{20}D$ 1.4860.

Anal. Calcd. for $C_{11}H_{15}Cl_3O_3$: C, 43.78; H, 5.00. Found: C, 43.79; H, 5.02.

1,1,1-Trichloro-3-octen-7-one (XXI).—Following the procedure of Pudovik,[9] *et al.*, 20 g. of XX (0.066 mole) was dissolved in 96 g. of water containing 4.8 g. of potassium hydroxide. The solution was stirred for 4 hr. at room temperature, then extracted with ether to remove the unchanged ester. The aqueous solution was treated with 15 ml. of 50% sulfuric acid and warmed for 30 min. in a hot water bath. The solution was then extracted with ether, the ether distilled and the product vacuum distilled. The main fraction, 11 g. (73%) distilled at 100–105° (0.8 mm.), $n^{20}D$ 1.4870.

Anal. Calcd. for $C_8H_{11}Cl_3O$: C, 41.81; H, 4.80. Found: C, 42.04; H, 4.80.

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(9) A. N. Pudovik and B. A. Arbuzov, *Bull. acad. sci. URSS, Classe sci. chim.*, 501 (1947); *Chem. Abstr.*, **42**, 1887b (1948).

3-Methyl-1-phenyl-4-(5,5,5-trichloro-2-pentenyl)-2-pyrazolin-5-one (XXII).—XX, 40 g. (0.133 mole), was mixed with 20 g. (0.184 mole) of phenylhydrazine and the solution heated for 6 hr. on a water bath. The solid that settled out upon cooling was filtered and gave a quantitative yield of crude material. The crude material was recrystallized from methanol; a solid, 33 g. (72%), melting at 128–130°, was isolated.

Anal. Calcd. for $C_{15}H_{15}Cl_3N_2O$: C, 52.00; H, 4.35. Found: C, 52.24; H, 4.52.

3-Methyl-1-*p*-nitrophenyl-4-(5,5,5-trichloro-2-pentenyl)-2-pyrazolin-5-one (XXIII).—XX, 35.7 g. (0.118 mole), was mixed with 19 g. (0.124 mole) of *p*-nitrophenylhydrazine. The mixture was heated for 6 hr. at a temperature of 100–110°. The crude solid that crystallized out upon standing overnight was recrystallized from methanol. The product, 30 g. (65%), melted at 148–150°.

Anal. Calcd. for $C_{15}H_{14}Cl_3N_3O_3$: C, 45.80; H, 3.59. Found: C, 45.70; H, 3.73.

1-Bromo-2,5,5,5-tetrachloro-3,4-bis(trichloromethylthio)-pentane (XXVIa) or 1-Bromo-3,5,5,5-tetrachloro-2,4-bis-(trichloromethylthio)pentane (XXVIb).—I, 59 g. (0.199 mole), was treated with 100 g. (0.508 mole) of perchloromethyl mercaptan for 96 hr. at a temperature from 92–130°. The excess perchloromethyl mercaptan was distilled at reduced pressure and the product, 60 g., was distilled under a vacuum. The main fraction, 30 g., distilled at 80° (0.1 mm.), $n^{20}D$ 1.5743. The elemental analysis was closer to that of XXVI than to that of bromotetrachloro(trichloromethylthio)pentane.

Anal. Calcd. for $C_7H_4BrCl_{10}S_2$: C, 14.30; H, 0.85; halogen as Cl, 66.50. Found: C, 13.97; H, 0.93; halogen as Cl, 66.0.

2,5,5,5-Tetrachloro-3,4-bis(trichloromethylthio)-1-pentyl-Acetate (XXVIIa) or 3,5,5,5-Tetrachloro-2,4-bis(trichloromethylthio)-1-pentyl Acetate (XXVIIb).—V, 55 g. (0.217 mole), was caused to react with 100 g. of perchloromethyl mercaptan (0.508 mole) at a temperature of 90–95° for 44 hr. The excess perchloromethyl mercaptan was distilled at reduced pressure and the product vacuum distilled. The first fraction, 30 g., distilled at 104–110° (2 mm.), $n^{20}D$ 1.5400. The second fraction, 37 g., distilled at 110–120° (2 mm.), $n^{20}D$ 1.5443. The fractions were redistilled; the first fraction distilled at 80–85° (0.1 mm.), $n^{20}D$ 1.5400, and the second fraction at 85–95° (0.1 mm.), $n^{20}D$ 1.5448.

The empirical formula of the first fraction was $C_9H_8Cl_{10}O_2S_2$: Calcd.: C, 19.2; H, 1.41; Cl, 62.9; S, 11.2. Found: C, 19.99; H, 1.71; Cl, 61.7; S, 11.80.

The empirical formula for the second fraction was $C_9H_8Cl_{10}O_2S_2$: Calcd.: C, 19.2; H, 1.41; Cl, 62.9; S, 11.2. Found: C, 19.17; H, 1.66; Cl, 61.4; S, 13.19.

5,5,5-Trichloro-2-pentenyl Esters or Ethers.—1-(2,4-Dichlorophenoxy)-5,5,5-trichloro-2-pentene (XXVIII), 5,5-5-trichloro-2-pentenyl benzoate (XXIX), and 5,5,5-trichloro-2-pentenyl butyrate (XXX) were prepared by the method outlined (see Table III).

Anhydrous potassium carbonate (0.25 mole) was added to a solution of the phenol or acid (*ca.* 0.25 mole) in ethyl methyl ketone (175 ml.). To this mixture was added I (0.255 mole) dropwise. The mixture was refluxed for 3 hr., cooled, and the potassium bromide filtered. The solvent was distilled at reduced pressure and the product vacuum distilled.

5,5,5-Trichloro-2-penten-1-ol (XXXI).—Anhydrous hydrogen chloride was bubbled into methanol (250 ml.) containing 76 g. (0.33 mole) of VI. The mixture was then refluxed for 2 hr., the solvent and methyl acetate distilled at reduced pressure leaving a quantitative crude yield of alcohol. The alcohol was vacuum distilled; the main product, 45 g. (73%), $n^{20}D$ 1.505, distilled at 80–87° (1 mm.). The analytical sample distilled at 82–83° (1 mm.).

Anal. Calcd. for $C_5H_7Cl_3O$: C, 31.60; H, 3.70. Found: C, 31.02; H, 3.82.

Bis-(5,5,5-trichloro-2-pentenyl) Ether (XXXII).—XXXI, 570 g. (3.0 moles), was treated with 12 g. of sodium hydroxide (0.30 mole). After all the sodium hydroxide had been dissolved, 178 g. (1.5 moles) of butadiene sulfone was added over a 2-hr. period. The mixture was then heated at 70° for 50 hr. The solution was poured into water and the organic layer separated and dried. The crude material was vacuum distilled; the main fraction was the unchanged alcohol. A liquid, 160 g., distilling at 110–170° (0.9 mm.) was next isolated. Upon redistilling this material a liquid, 100 g. distilled at 164–167° (0.9 mm.) $n^{20}D$ 1.4211, was isolated.

Anal. Calcd. for $C_{10}H_{12}Cl_6O$: C, 33.30; H, 3.33. Found: C, 33.61; H, 3.48.

5,5,5-Trichloro-2-pentenyl Esters.—5,5,5-Trichloro-2-pentenyl trichloroacetate (XXXIII), 5,5,5-trichloro-2-pentenyl *p*-nitrobenzoate (XXXIV), and 5,5,5-trichloro-2-pentenyl 3,5-dinitrobenzoate (XXXV) were prepared by the following procedure (see Table III).

The acid chloride, approximately 0.125 mole, was heated with 0.130 mole of the alcohol XXXI, on a hot water bath for 2 hr. The ester was vacuum distilled, if a liquid, or recrystallized from ethanol, if a solid.

5,5,5-Trichloro-2-pentenyl N,N-Diethyl Dithiocarbamate (XXV).—Diethylamine, 25 g. (0.343 mole), was added dropwise to 27 g. (0.355 mole) of carbon disulfide which had previously been cooled to 0°. To this solution was added dropwise a solution of 16 g. (0.40 mole) of sodium hydroxide in 50 ml. of water. After all the caustic had been added, 87 g. (0.345 mole) of I was added dropwise. The solution was slowly brought up to room temperature and finally heated to reflux for 4 hr. The solution was cooled and poured into water; the organic layer separated, and the aqueous layer extracted with chloroform. The combined organic and chloroform layers were dried over magnesium sulfate and filtered; the chloroform was distilled at reduced pressure leaving 76 g. (69.5%) of an oil. The last traces of solvent were removed from the oil by means of a high vacuum pump.

Anal. Calcd. for $C_{10}H_{16}Cl_3NS_2$: C, 37.57; H, 5.00 Found: C, 38.08; H, 5.19.

5,5,5-Trichloro-2-pentenyl Ethyl Carbonate (XL).—Ethyl chloroformate, 35 g. (0.324 mole), was added dropwise to 50 g. (0.265 mole) of the alcohol XXXI. After all of the ethyl chloroformate had been added, the solution was heated on a hot bath for 6 hr. The material was vacuum distilled; the unchanged alcohol and chloroformate distilled between 70–100° (2 mm.) The second fraction, 26 g., distilled at 100–120° (2 mm.). The second fraction was redistilled and a product, 24 g. (35%), $n^{20}D$ 1.4825, distilled at 110° (0.4 mm.).

Anal. Calcd. for $C_8H_{11}Cl_3O_3$: C, 36.76; H, 4.23. Found C, 36.59; H, 4.30.

5,5,5-Trichloro-2-pentenyl Chloroformate (XLI).—XXXI, 34 g. (0.180 mole), was caused to react with excess phosgene gas. The addition was terminated when the exothermic reaction had subsided. The excess phosgene was swept out of the system with dry nitrogen, the residue was washed with water and separated. The residue was dried over sodium sulfate and vacuum distilled. The main fraction, 42 g. (93%), distilled at 74–76° (0.4 mm.), $n^{20}D$ 1.4970.

Anal. Calcd. for $C_8H_6Cl_4O_2$: C, 28.60; H, 2.38. Found: C, 28.51; H, 2.47.

5,5,5-Trichloro-2-pentenyl Carbamates.—5,5,5-Trichloro-2-pentenyl carbamate (XLII), 5,5,5-trichloro-2-pentenyl *N*-methylcarbamate (XLIII), 5,5,5-trichloro-2-pentenyl N,N-dimethylcarbamate (XLIV), and 5,5,5-trichloro-2-pentenyl N,N'-diethylcarbamate (XLV) were prepared by the method outlined (see Table IV).

Approximately 0.218 mole of the chloroformate XLI was dissolved in 70 ml. of carbon tetrachloride. The liquid amine (0.436 mole) was added dropwise, or if the amine was a gas it was bubbled into the solution. After the amine had been added, the solution was heated on a hot water

bath for 2–3 hr. The amine hydrochloride was filtered and the solvent distilled at reduced pressure. The product, if a liquid, was vacuum distilled; if a solid, it was recrystallized from the appropriate solvent.

5,5,5-Trichloro-2-pentenyl Carbamates.—5,5,5-Trichloro-2-pentenyl N-butylcarbamate (XXXVI), 5,5,5-trichloro-2-pentenyl N-propylcarbamate (XXXVII), 5,5,5-trichloro-2-pentenyl N-(1-methylpropyl) carbamate (XXXVIII), and 5,5,5-trichloro-2-pentenyl N-phenylcarbamate (XXXIX) were prepared by the method outlined (see Table IV).

Approximately 50 g. of the isocyanate was added dropwise to 0.370 mole of XXXI. After all the isocyanate had been added, the solution was heated on a hot water bath for 1 hr. and finally at 110° for 4 hr. The mixture was then vacuum distilled and the product isolated. If the carbamate was a solid it was recrystallized from the appropriate solvent.

5,5,5-Trichloro-2-pentenyl Carbanilates.—5,5,5-Trichloro-2-pentenyl 2-chlorocarbanilate (XLVI), 5,5,5-trichloro-2-pentenyl 2,4-dichlorocarbanilate (XLVII), and 5,5,5-trichloro-2-pentenyl 2,4,6-trichlorocarbanilate (XLVIII) were prepared by the method outlined (see Table IV).

Approximately 0.200 mole of the amine was dissolved in 50 ml. of acetone. To this solution was added dropwise 0.1 mole of the chloroformate XLI. After all the chloroformate had been added, the solution was refluxed for 2 hr. The amine hydrochloride was filtered and washed with acetone. The acetone was distilled and the residue extracted with water. The organic layer was separated and the aqueous layer extracted with chloroform. The combined crude carbanilate and chloroform solution was dried over magnesium sulfate, filtered, and the solvent removed under reduced pressure. An attempt to vacuum distill a small portion of the liquid carbamates resulted in decomposition. The last traces of solvent were removed with a high vacuum pump. The solid carbanilates were recrystallized from appropriate solvents.

5,5,5-Trichloro-2-pentenyl Ester of the Anhydrosulfide of Thiol Carbonic Acid and O,O-Diethyl Phosphorodithioic Acid (XLIX).—Ammonium O,O-diethyl phosphorodithioate, 41 g. (0.2 mole), was dissolved in 175 ml. of acetone. To this solution was added dropwise 50.4 g. (0.20 mole) of the chloroformate XLI. The temperature of the reaction rose slowly from 24° to a maximum of 35°. After all the chloroformate had been added, the solution was heated on a water bath for 2 hr. After cooling, the solid was filtered and washed with acetone. The acetone was distilled at reduced pressure and the last traces of solvent removed with a vacuum pump. The crude product weighed 61 g. (76%).

Anal. Calcd. for $C_{10}H_{16}Cl_3O_4PS_2$: C, 30.00; H, 4.00; P, 7.50. Found: C, 29.97; H, 4.05; P, 8.10.

5,5,5-Trichloro-2-pentenyl Allophanate (L).—Following the procedure of Dains,[10] *et al.*, XLI, 25.2 g. (0.1 mole) was added to 12.6 g. (0.21 mole) of urea. This mixture was heated on a water bath for 3 hr. The solid isolated was washed with water and then with heptane. The crude solid was recrystallized from methanol; the product 12 g. (44%), melted at 182–183°.[11]

Anal. Calcd. for $C_7H_9Cl_3N_2O_3$: C, 30.40; H, 3.26. Found: C, 30.42; H, 3.25.

(10) F. B. Dains and E. Wertheim, *J. Am. Chem. Soc.*, **42**, 2303 (1920).

(11) All melting points are uncorrected. Elemental and infrared analyses by Diamond Alkali Co. Research Analytical Laboratory.

The Preparation of Succinamido Peptides[1]

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The introduction of cystine as a linkage in polypeptidic structures is not without difficulties. Assuming that, in a number of cases where cystine is present in the natural peptide, it plays no specific pharmacodynamic role, some other residue might well be able to replace cystine, without altering the characteristic activity of the peptide. Succinic acid seemed particularly attractive as a replacement for cystine. The present paper describes the preparation of symmetric and mixed succinamido peptides. The method may well be capable of being extended to the preparation of more complex structures, which are perhaps biologically interchangeable with natural cystine.

Compounds where a dicarboxylic acid is linked with two amino acids through their amino groups, or compounds where a diamine is linked to two amino acids through their carboxylic groups are known in nature. Such a combination offers a wide range of possibilities from the point of view of synthesis. However, it appears that only a few such compounds have been described in the literature, *e.g.*, the derivatives of oxalic, succinic, and adipic acids.[2-8] The recent publication of Schröder, Klieger, and Gibian[9] reports more syntheses of this class of compounds. In addition, a number of succinimides have been synthesized: *e.g.* succinimidoglycine,[6,10] succinimido-DL-alanine,[6] succinimido-L-leucine,[6] and succinimido-L-valine.[6] Also a number of β-carboxypropionylamino acids have been synthesized, for example β-carboxypropionylglycine, β-carboxypropionyl-L-leucine, and β-carboxypropionyl-DL-alanine.[6]

We have been particularly interested in the preparation of compounds where the two carboxylic groups of succinic acid are linked to the basic

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(8) G. Faust and M. Klepel, *J. prakt. Chem.* [4], **11**, 133 (1960).

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