Anal. Calcd. for $C_{19}H_{20}O$: C, 86.32; H, 7.63. Found: C, 86.42; H, 7.61.

Carbon–hydrogen analysis and the infrared spectrum showed the 139.5–142° compound to be a mixture of the two isomers IIIa and IIIb.

Anal. Calcd. for $C_{19}H_{22}O_2$: C, 80.81; H, 7.85. Found: C, 81.05; H, 8.00.

***trans*-2-(α-Hydroxybenzhydryl)-cyclohexanol (IIIb).**—The same procedure used in the preparation of IIIa applied here to 5.0 g. of *trans*-methyl-2-hydroxycyclohexanecarboxylate yielded after recrystallization only 0.30 g. of IIIb, m.p. 161–162°.

Anal. Calcd. for $C_{19}H_{22}O_2$: C, 80.81; H, 7.85. Found: C, 80.88; H, 7.96.

Also isolated was 0.60 g. of a compound, m.p. 131–133° (m.p. not changed by further recrystallization) whose analysis and infrared spectrum showed it to be either a crystalline modification of IIIb or IIIb with a depressed melting point due to a small amount of impurity not removed by recrystallization and not apparent in the infrared spectrum.

Anal. Calcd. for $C_{19}H_{22}O_2$: C, 80.81; H, 7.85. Found: C, 80.60; H, 7.91.

Addition of 15.8 g. (0.1 mole) of *trans*-methyl 2-hydroxycyclohexanecarboxylate (IIb) in 50 ml. ether to 0.5 mole of phenyllithium in 300 ml. of ether was made with stirring over 2.25 hours. The crude yield of IIIb weighed 24.6 g. Several recrystallizations yielded 20.8 g., m.p. 160.5–161.0°.

***cis*- and *trans*-Isopulegol Hydrate (Va) and (Vb). Internal Prins Reaction of *d*-Citronellal.**—Two hundred grams of *d*-citronellal (Matheson Co.), $[\alpha]^{24}D$ 10.4°, was stirred with 1000 ml. of 5% sulfuric acid at room temperature for 27 hours. Some cooling was necessary initially. The organic phase was removed with ether and the ether extracts were washed with water and then 5% sodium carbonate and finally dried over sodium sulfate. The ether was removed and the residual water removed by distillation with benzene. The remaining thick oil was distilled to give 180 ml., b.p. 102–106° at 0.3–0.6 mm. This was fractionated in a 2-foot Stedman column (approx. 50 theor. plates) to give sixteen fractions. Fractions 3 to 11 (b.p. 129–133° at 5 mm.) and also 13 to 15 (b.p. 136–142° at 5 mm.) solidified. The infrared spectra of all the former (3 to 11) were identical and of all the latter (13 to 15) corresponded to a different homogeneous compound. Recrystallization of the former yielded pure *cis*-isopulegol hydrate, m.p. 61–62° (this isomer was obtained under different circumstances by Prins[12]). The latter gave *trans*-isopulegol. The yields were 90.86 g. of the *cis* compound, m.p. 61–62°, and only 39.86 g. of the *trans* isomer, m.p. 75°. Fraction 16 (b.p. 142° at 5 mm.) was slightly oily; it weighed 3.10 g. and yielded only the isomer m.p. 75° on recrystallization.

Anal. Va Calcd. for $C_{19}H_{20}O_2$: C, 69.72; H, 11.70. Found: C, 69.84; H, 11.88. *Anal.* Vb Calcd. for $C_{10}H_{22}O_2$: C, 69.72; H, 11.70. Found: C, 69.50; H, 11.90.

Infrared spectra were obtained with a Perkin–Elmer model 21 spectrophotometer in chloroform solution. Spectra in the 2–3 μ region in dilute solution were run in carbon tetrachloride at 0.005 *M* except for compound IIIa which was run at 0.002 *M*. A 23-mm. glass cell equipped with NaCl plates was used. The accuracy varies from ±1 cm.$^{-1}$ for the sharp free OH bands to a slightly greater error in the case of the broader bonded OH bands.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE AVERY LABORATORY OF THE UNIVERSITY OF NEBRASKA]

Studies in the Furan Series. Chloralfuramides and Some of their Reactions

BY JOE R. WILLARD[1] AND CLIFF S. HAMILTON

RECEIVED DECEMBER 13, 1952

2-Furamide, 5-bromo-2-furamide, 5-methyl-2-furamide, 5-nitro-2-furamide, 5-*t*-butyl-2-furamide and β-(2-furyl)-acrylamide were added to chloral to form the corresponding 1-(amido)-2,2,2-trichloroethanols. The benzoates of 1-(2-furamido)- and 1-(5-bromo-2-furamido)-2,2,2-trichloroethanols were prepared. 1-(2-Furamido)-, 1-(5-bromo-2-furamido)-, 1-(5-nitro-2-furamido)- and 1-(5-*t*-butyl-2-furamido)-2,2,2-trichloroethanols reacted with phosphorus pentachloride to give the corresponding 1-(furamido)-1,2,2,2-tetrachloroethanes. These tetrachloroethanes were then treated with various alcohols, ammonia and amines to yield the corresponding 1-(furamido)-1-alkoxy-, -1-amino-, -1-arylamino- and -1-alkylamino-2,2,2-trichloroethanes. Reaction of 1-(2-furamido)- and 1-(5-bromo-2-furamido)-1,2,2,2-tetrachloroethanes with ammonia gave the corresponding bis-(1-furamido-2,2,2-trichloroethyl)-amines.

While the reaction of amides with chloral has been known for a long time and many "chloralamides" have been prepared,[2] no heterocyclic amides have been added to chloral. Therefore, the addition of some 2-furamides to chloral was investigated and some studies of the resulting chloralfuramides were made.

2-Furamide, 5-bromo-2-furamide, 5-methyl-2-furamide, 5-nitro-2-furamide, 5-*t*-butyl-2-furamide and β-(2-furyl)-acrylamide reacted readily with anhydrous chloral in the absence of catalysts to give a stable crystalline solid in each case. The properties of these chloralamides are indicated in Table I.

As was reported by Chattaway[3] in studies on monosubstituted ureas, N-substituted furamides (N-benzyl- and N-methyl-2-furamide) did not react under the conditions employed for the above amides.

While many chloralamides have been acylated by the action of benzoyl chloride in 10% aqueous sodium hydroxide,[4] this method was not successful in the case of 1-(2-furamido)- or 1-(5-bromo-2-furamido)-2,2,2-trichloroethanol. The benzoyl derivatives of the latter compounds were, however, obtained by the action of benzoyl chloride in excess pyridine. Attempts to acetylate these chloralfuramides using acetic anhydride with excess pyridine, aqueous sodium hydroxide or sodium acetate solution were unsuccessful, yielding only unreacted starting material, non-crystallizable oil or the corresponding furoic acid. Similarly, attempts to methylate the chloralfuramides using dimethyl sulfate in excess aqueous sodium acetate or sodium hydroxide solution yielded only unreacted starting material or the corresponding furoic acid.

The chlorination of the 1-(furamido)-2,2,2-

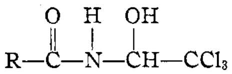
(1) Parke, Davis and Company Fellow. Present address: Research and Development Department, Westvaco Chemical Division, Food Machinery and Chemical Corp., So. Charleston, W. Va.

(2) A. N. Meldrum and M. J. Bhojraj, *J. Indian Chem. Soc.*, **13**, 185 (1936); N. W. Hirwe, *J. Univ. Bombay*, **6II**, 182 (1937).

(3) F. D. Chattaway and E. J. James, *Proc. Roy. Soc.* (*London*), **A134**, 372 (1931).

(4) N. W. Hirwe and K. D. Gavankar, *J. Univ. Bombay*, **6II**, 123 (1937).

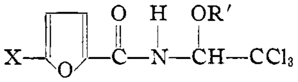
TABLE I



$$R{-}C(=O){-}N(H){-}CH(OH){-}CCl_3$$

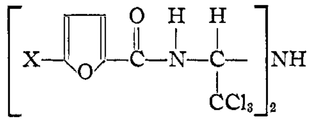
R	Procedure	M.p., °C.	Yield, %	Recrystn. solv.	Formula	Color	Heating time, min.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
2-Furyl	A	153–154	86	Ethanol	$C_7H_6O_3NCl_3$	White	10	32.53	32.30	2.34	2.48	5.42	5.21
5-Bromo-2-furyl	A	159–160	84	Ethanol	$C_7H_5O_3NCl_3Br$	White	15	24.92	25.10	1.49	1.81	4.15	4.14
5-Nitro-2-furyl	A	153.5–154.5	64	Ethanol	$C_7H_5O_5N_2Cl_3$	Pale yellow	15	27.70	27.69	1.66	2.02	9.23	9.14
5-*t*-Butyl-2-furyl	A	146–147	91	Methanol	$C_{11}H_{14}O_3NCl_3$	White	15	42.00	42.05	4.49	4.47	4.45	4.68
5-Methyl-2-furyl	A	151–152	74	EtOH–H_2O	$C_8H_8O_3NCl_3$	White	5	35.35	35.17	2.96	3.31	5.22	5.58
β-(2-Furyl)-vinyl	A	155–157	30	Ethanol	$C_9H_8O_3NCl_3$	Tan	10	38.00	38.27	2.86	3.13	4.93	4.94

TABLE II



X	R′	Procedure	M.p., °C.	Yield, %	Recrystn. solv.	Formula	Color	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
H	Bz	B	162–163.5	60	Ethanol	$C_{14}H_{10}O_4NCl_3$	White	46.38	46.65	2.78	2.99	3.69	4.00
Br	Bz	B	146–147	43	Benzene–pet. ether	$C_{14}H_9O_4NCl_3Br$	White	38.09	38.24	2.06	2.21	3.18	3.12
H	CH_3	C	84–85	80	Methanol–water	$C_8H_8O_3NCl_3$	White	35.25	35.15	2.96	3.20	5.14	5.43
Br	CH_3	C	99–100.5	92	Ethyl acetate–pet. ether	$C_8H_7O_3NCl_3Br$	White	27.34	27.71	2.01	2.48	3.98	4.27
$(CH_3)_3$–C	CH_3	C	98–99	100	Ethyl acetate–pet. ether	$C_{12}H_{16}O_3NCl_3$	White	43.85	44.12	4.91	5.24		
O_2N	CH_3	C	103–104	57	Ethyl acetate–pet. ether	$C_8H_7O_5N_2Cl_3$	Pale yellow	30.25	30.37	2.22	2.38	8.83	8.80
H	C_2H_6	C	81–82	70	Ethyl acetate–pet. ether	$C_9H_{10}O_3NCl_3$	White	37.72	38.08	3.52	3.57	4.89	4.99

TABLE III



X	Procedure	M.p., °C.	Yield, %	Recrystn. solv.	Formula	Color	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
H	D	222–224	37	Ethanol	$C_{14}H_{11}O_4N_3Cl_6$	White	33.77	33.79	2.27	2.39	8.44	8.37
Br	D	215–216	14	Ethanol	$C_{14}H_9O_4N_3Cl_6Br_2$	White	25.64	25.55	1.39	1.60	6.41	6.38

trichloroethanols using phosphorus pentachloride proceeded readily to give the corresponding 1,2,2,2-tetrachloroethanes.[5] The tetrachloroethanes from 1-(2-furamido)-, 1-(5-bromo-2-furamido)- and 1-(5-nitro-2-furamido)-2,2,2-trichloroethanols were obtained as tan solids which turned brown very rapidly when in the solid form. Absence of air or light did not appear to reduce the rate of decomposition. Repeated attempts to purify the chloro compounds were unsuccessful and they were either used at once or stored as dry ether solutions.

As mentioned previously, attempts to methylate the trichloroethanols using dimethyl sulfate were unsuccessful. However, the chloro derivatives from 1-(5-bromo-2-furamido)-, 1-(5-nitro-2-furamido)- and 1-(5-*t*-butyl-2-furamido)-2,2,2-trichloroethanols were treated with methanol and that from 1-(2-furamido)-2,2,2-trichloroethanol with methanol and ethanol to give the corresponding -1-alkoxy-2,2,2-trichloroethanes.

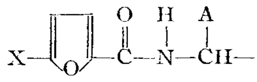
The chloro derivatives reacted quite readily with ammonia. In attempts to prepare the trichloroethylamino analogs, the tetrachloroethanes derived from 1-(2-furamido)- and 1-(5-bromo-2-furamido)-2,2,2-trichloroethanol were added to excess ammonium hydroxide and to excess ethanolic ammonia. In each case, the major product was not the desired amidotrichloroethylamine, but the bis-(furamidotrichloroethyl)-amine. The desired 1-(2-furamido)-2,2,2-trichloroethylamine was obtained in good yield by treating a saturated solution of ammonia in ether with a dry ether solution of 1-(2-furamido)-1,2,2,2-tetrachloroethane.

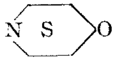
Reaction of these tetrachloroethanes with amines proceeded readily to give the corresponding 1-furamido-1-amino-2,2,2-trichloroethanes. 1-(2-Furamido)-1,2,2,2-tetrachloroethane was treated with aniline, benzylamine, β-phenylethylamine, piperidine, morpholine and methylamine. 1-(5-Bromo-2-furamido)-1,2,2,2-tetrachloroethane and 1-(5-nitro-2-furamido)-1,2,2,2-tetrachloroethane reacted with aniline and benzylamine and 1-(5-*t*-butyl-2-furamido)-1,2,2,2-tetrachloroethane with benzylamine. All the derivatives were obtained as white or very pale yellow crystalline solids except 1-(5-nitro-2-furamido)-1-phenylamino-2,2,2-trichloroethane which was bright yellow-orange.

---

[5] A. N. Meldrum and G. M. Vad, *J. Indian Chem. Soc.*, **13**, 117 (1936).

TABLE IV



X	A	Procedure	M.p., °C.	Yield, %	Recrystn. solv.	Formula	Color	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
H	H-N-C_6H_5	E	162–163	50	Ethanol	$C_{13}H_{11}O_2N_2Cl_3$	White	46.78	47.03	3.32	3.52	8.40	8.26
Br	H-N-C_6H_5	E	181–182.5	60	Ethanol	$C_{13}H_{10}O_2N_2Cl_3Br$	White	37.84	38.05	2.45	2.65	6.80	7.19
H	H-N-CH_2-C_6H_5	F	132.5–133.5	30	Ethyl acetate–pet. ether	$C_{14}H_{12}O_2N_2Cl_3$	White	48.37	48.60	3.77	3.81	8.03	8.05
Br	H-N-CH_2-C_6H_5	F	136.5–138	75	Ethyl acetate–pet. ether	$C_{14}H_{12}O_2N_2Cl_3Br$	White	39.41	39.53	2.84	2.84	6.61	6.61
NO_2	H-N-CH_2-C_6H_5	F	169–171	45	Ethyl acetate–pet. ether	$C_{14}H_{12}O_4N_3Cl_3$	Pale yellow	42.82	42.98	3.08	3.24	10.70	10.66
$C(CH_3)_3$	H-N-CH_2-C_6H_5	F	176–177	63	Ethyl acetate–pet. ether	$C_{18}H_{20}O_2N_2Cl_3$	White	53.54	53.39	5.25	5.48		
H	H-N-CH_2-CH_2-C_6H_5	F	120.5–121.5	55	Ethyl acetate–pet. ether	$C_{15}H_{14}O_2N_2Cl_3$	White	49.80	49.54	4.18	4.41	7.71	7.67
H		F	102–103	55	Ethyl acetate–pet. ether	$C_{12}H_{15}O_2N_2Cl_3$	White	44.27	44.53	4.65	4.71	8.61	8.69
H		F	94.5–96	49	Ethyl acetate–pet. ether	$C_{11}H_{13}O_3N_2Cl_3$	White	40.33	40.60	4.00	3.80	8.52	8.56
H	N-CH_3	D	120–121	18	Ethyl acetate–pet. ether	$C_8H_9O_2N_2Cl_3$	Tan	35.38	35.59	3.35	3.79	10.32	10.22

Repeated attempts to obtain characterizable products from the reaction of 1-(2-furamido)-1,2,2,2-tetrachloroethane with diethylaminoethylamine and dimethylaminopropylamine were unsuccessful.

Experimental

Preparation of Amides. 2-Furamide.—This amide was obtained in quantitative yield by slow addition of 2-furoyl chloride to excess cold ammonium hydroxide; it melted at 139–141° without recrystallization (reported[6] m.p. 142–143°).

5-Bromo-2-furamide.—5-Bromo-2-furoic acid, melting at 180–182° (reported[7] m.p. 184°), was prepared in 62% yield by bromination of 2-furoic acid according to the method of Whittaker.[7] The acid was converted by excess thionyl chloride into the acid chloride in 78% yield. 5-Bromo-2-furamide was obtained in the calculated yield as described for 2-furamide; it melted at 145–146.5° (reported[8] m.p. 145°).

5-Methyl-2-furamide.—5-Methyl-2-acetylfuran was prepared in 40% yield by acetylation of 2-methylfuran in the presence of boron trifluoride according to the method of Farrar and Levine.[9] Oxidation of this ketone by potassium hypochlorite[10] gave, in 25% yield, 5-methyl-2-furoic acid which melted at 106–107° (reported[6] m.p. 108–109°). The acid was converted to the acid chloride by heating with excess thionyl chloride and an ether solution of the acid chloride was treated with an excess of dry ammonia gas to give, in 69% yield (based on acid), 5-methyl-2-furamide which melted at 130–131.5° (reported[11] m.p. 132°).

5-Nitro-2-furamide.—5-Nitro-2-furamide was prepared from methyl 2-furoate according to the method of Marquis.[12] The over-all yield for the five-step process was 43% of amide which melted at 159–160° (reported[13] m.p. 161°).

5-*t*-Butyl-2-furamide.—Ethyl 2-furoate was alkylated according to the method of Gilman and Calloway[14] to give 70–75% of ethyl 5-*t*-butyl-2-furoate. Hydrolysis of the ester with ethanolic potassium hydroxide gave 85–90% of 5-*t*-butyl-2-furoic acid which melted at 102–104° (reported[14] m.p. 104–105°). The acid was converted to the chloride in 80–85% yield by the action of thionyl chloride. An ether solution of 5-*t*-butyl-2-furoyl chloride was treated with dry ammonia to give 80–95% yield of white 5-*t*-butyl-2-furamide which melted at 121–123°.[15]

Anal. Calcd. for $C_9H_{13}O_2N$: C, 64.65; H, 7.84; N, 8.38. Found: C, 64.83; H, 8.23; N, 8.28.

β-(2-Furyl)-acrylamide.—β-(2-Furyl)-acrylic acid which melted at 138–140° (reported[6] m.p. 141°) was prepared from 2-furfural in 89% yield according to the procedure of Rajagopalan.[16] A dry benzene solution of the acid was heated with a slight excess of thionyl chloride and, after 3 hours at the reflux temperature, the entire mixture was poured into excess aqueous ammonium hydroxide to give β-(2-furyl)-acrylamide, which melted at 165–167° (reported[6] m.p. 168–169°), in 54% yield.

Reaction of Amides with Chloral; Formation of 1-(Substituted)-2,2,2-trichloroethanol (General Procedure A).—

---

[6] E. Huntress and R. Mulliken, "Identification of Pure Organic Compounds, Order I," John Wiley and Sons, Inc., New York, N. Y., 1941.

[7] R. M. Whittaker, *Rec. trav. chim.*, **52**, 352 (1933).

[8] H. B. Hill and C. R. Sanger, *Ann.*, **232**, 52 (1886).

[9] M. W. Farrar and R. Levine, THIS JOURNAL, **72**, 3695 (1950).

[10] *Ibid.*, **71**, 1496 (1949).

[11] R. Kuhn, F. Kohler and L. Kohler, *Z. physiol. Chem.*, **247**, 197 (1937); *C. A.*, **31**, 6264 (1937).

[12] R. Marquis, *Ann. chim. phys.*, [8] **4**, 196 (1904).

[13] H. Gilman and Yale (THIS JOURNAL, **72**, 3593 (1950)) reported preparation of 5-nitro-2-furamide by the action of aqueous ammonium hydroxide on 5-nitro-2-furoyl chloride; however, they did not report the yield. It has been our experience that any attempt to treat a nitrofuran with aqueous ammonia will result in extensive decomposition of the nitro compound.

[14] H. Gilman and N. O. Calloway, THIS JOURNAL, **55**, 4197 (1933).

[15] An attempt to prepare this amide by ammonolysis of ethyl 5-*t*-butyl-2-furoate by the action of excess concentrated ammonium hydroxide solution was unsuccessful, the ester being recovered quantitatively after six weeks at room temperature.

[16] S. Rajagopalan and P. Raman, *Org. Syntheses*, **25**, 51 (1945).

The amide (1 equivalent) was mixed, in a flask equipped with a reflux condenser, with anhydrous chloral (1.2–2.0 equivalents) and the mixture was heated under gentle reflux until a homogeneous mixture was obtained. Heating was continued until solid began to separate, the length of this heating period varying for the different amides. After cooling to room temperature, the solid mass was recrystallized from an appropriate solvent until the melting point remained constant (see Table I for the properties of the chloralamides).

Benzoylation of 1-(Furamido)-2,2,2-trichloroethanols (General Procedure B).—Solid 1-furamido-2,2,2-trichloroethanol (1 equivalent) was added to a solution of benzoyl chloride (2 equivalents) in excess pyridine. After 5–10 minutes, the mixture was poured into crushed ice and the aqueous mixture set aside for 24 hours. The crude solid was recrystallized from an appropriate solvent until the melting point was constant (see Table II).

Chlorination of 1-(Furamido)-2,2,2-trichloroethanols.—According to a modification of the method of Hirwe and Deshpandi,[17] the furamidotrichloroethanol was mixed, in a flask equipped with a reflux condenser, with an equimolar quantity of phosphorus pentachloride. The mixture was warmed very gently to initiate reaction and the source of heat was removed as soon as reaction began. When the vigorous initial reaction had subsided, the mixture was warmed very gently until a homogeneous liquid was obtained. The clear liquid was poured into three times its weight of crushed ice and the aqueous mixture was treated according to one of the following procedures.

Alkoxylation of 1-(Furamido)-1,2,2,2-tetrachloroethanes (General Procedure C).—The supernatant liquid was decanted from the insoluble oily tetrachloroethane and the oil was washed thoroughly with cold water. The oil was immediately dissolved in an excess of the appropriate alcohol and the solution was heated under reflux for 5 hours. The hot mixture was poured into excess ice-water, the oil isolated and treated further as was appropriate (see Table II).

Ammoniation of 1-(Furamido)-1,2,2,2-tetrachloroethanes (General Procedure D).—The aqueous mixture was extracted with four 50-ml. volumes of ether. The ether extracts were combined and added, without preliminary drying, to excess concentrated ammonium hydroxide or 33% aqueous methylamine. The mixture was shaken vigorously for 5 minutes. The layers were separated and the ethereal layer was concentrated by removal of the ether under reduced pressure. The residue was recrystallized from an appropriate solvent until the melting point was constant (see Table III).

Amination of 1-(Furamido)-1,2,2,2-tetrachloroethanes (General Procedure F).—The aqueous mixture was extracted with four 50-ml. volumes of ether, the ether extracts were combined and dried over magnesium sulfate. The magnesium sulfate was removed by filtration and the dry ether solution was chilled in an ice-bath. To the cold solution was added very slowly an excess (2.1 molecular equivalents) of the appropriate amine. The separated solid was removed by filtration and the filtrate was concentrated by distillation of the ether under reduced pressure. The residual solid was recrystallized from an appropriate solvent until the melting point was constant.

Ammoniation of 1-(2-Furamido)-1,2,2,2-tetrachloroethane; 1-(2-Furamido)-2,2,2-trichloroethylamine.—The aqueous mixture from chlorination of 20 g. (0.08 mole) of 1-(2-furamido)-2,2,2-trichloroethanol was extracted with four 100-ml. volumes of dry ether and the combined ether extracts were dried over magnesium sulfate.

In a 1-liter, 3-necked flask, fitted with a gas inlet tube and mechanical stirrer, and surrounded by an ice-bath, was placed 300 ml. of dry ether. Dry ammonia gas was passed into the ether for 15 minutes. While ammonia continued to pass through the well-stirred mixture, the previously prepared ether solution of the tetrachloro compound was added slowly, 1.5 hours being required to complete the addition.

The reaction mixture was subjected to filtration and the isolated solids were triturated with 100 ml. of dry ether. The combined filtrates were concentrated by distillation of the ether under reduced pressure. The residual solid, which weighed 12.5 g. (62%), melted at 77–80°. Four recrystallizations from a mixture of ethyl acetate and petroleum ether gave pale tan crystals which melted at 102.5–104°.

Anal. Calcd. for $C_7H_7O_2N_2Cl_3$: C, 32.64; H, 2.84; N, 10.88. Found: C, 32.79; H, 2.70; N, 10.63.

Treatment of an acidified ethanolic solution of this trichloroethylamine with an aqueous solution of sodium nitrite resulted in evolution of a gas and separation of the original trichloroethanol (identified by mixed melting point).

Phenylamination of 1-(5-Nitro-2-furamido)-1,2,2,2-tetrachloroethane; 1-(5-Nitro-2-furamido)-1-phenylamino-2,2,2-trichloroethane.—Eight grams (0.03 mole) of 1-(5-nitro-2-furamido)-2,2,2-trichloroethanol was chlorinated as described above. The supernatant liquid was decanted from the solid tetrachloro compound. The solid was dissolved in 20 ml. of acetone and to the acetone solution was added carefully 15 g. (0.16 mole) of aniline. The hot mixture was poured into 150 ml. of cold water and the aqueous mixture was set aside for 24 hours. The solid was isolated to give 10.7 g. (100%) of orange solid which melted at 170–178° (dec.).

Recrystallization from glacial acetic acid gave bright yellow-orange crystals which melted at 195–196° (bath preheated to 185°).

Anal. Calcd. for $C_{13}H_{11}O_4N_3Cl_3$: C, 41.36; H, 2.67; N, 11.10. Found: C, 41.54; H, 2.86; N, 11.21.

LINCOLN 8, NEBRASKA

---

[17] N. W. Hirwe and J. S. Deshpandi, *Proc. Ind. Acad. Sci.*, **13A**, 277 (1941).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

Ethylene Glycol Ethers of Pentaerythritol

BY STANLEY WAWZONEK AND COSTAS ISSIDORIDES[1]

RECEIVED NOVEMBER 17, 1952

The Tollens condensation of acetaldehyde and formaldehyde in 50% ethylene glycol yields pentaerythritol and the monoethylene glycol and the bis-(ethylene glycol) ethers of pentaerythritol. The structures of the last two compounds were demonstrated by synthesis from 3,3-bis-(hydroxymethyl)-oxacyclobutane and 2,6-dioxaspiro[3,3]heptane, respectively.

In a previous work[2] on the mechanism of the formation of dipentaerythritol in the preparation of pentaerythritol by the Tollens condensation, it was found that the methyl and dimethyl ethers of pentaerythritol could be made by running the condensation in 50% methanol.

The work has now been extended to a study of the condensation in 50% ethylene glycol to determine whether an ether I of the dipentaerythrityl type could be formed in this bifunctional solvent.

$$(HOCH_2)_3CCH_2OCH_2CH_2OCH_2C(CH_2OH)_3$$

I

When the Tollens condensation was carried out in the usual manner[2] and the products separated as the propionates, the main product after saponification was pentaerythritol. Other compounds

---

[1] Abstracted in part from the Ph.D. thesis of Costas Issidorides, February, 1953.

[2] S. Wawzonek and D. A. Rees, THIS JOURNAL, **70**, 2433 (1948).