Table II. 4,4,4-Trichloro-1-amino-2-butanol Hydrochlorides

$Cl_3CCH_2CH(OH)CH_2NR^1R^2 \cdot HCl$

Compd. No.	R^1	R^2	M.P.[a], °C.	Yield,[b] %	Molecular Formula
19	Iso-C_3H_7	H	203	73	$C_7H_{15}Cl_4NO$
20	*n*-C_4H_9	H	230	51	$C_8H_{17}Cl_4NO$
21	*sec*-C_4H_9	H	190	68	$C_8H_{17}Cl_4NO$
22	Iso-C_4H_9	H	224	62	$C_8H_{17}Cl_4NO$
23	*tert*-C_4H_9	H	212	58	$C_8H_{17}Cl_4NO$
24	$\underbrace{CH_2(CH_2)_4CH}$—	H	225	71	$C_{10}H_{19}Cl_4NO$
25	Iso-C_3H_7	Iso-C_3H_7	177	39	$C_{10}H_{21}Cl_4NO$
26	—CH_2CH_2—O—CH_2CH_2—		182	50	$C_8H_{15}Cl_4NO_2$
27	—$CH_2CH_2CH_2CH_2CH_2$—		191	52	$C_9H_{17}Cl_4NO$

[a] All m.p. for analytical samples; all products melted with decomposition. [b] Yields for recrystallized products.

EXPERIMENTAL

Allyl glycidyl ether was obtained from Matheson, Coleman and Bell and used as received. 4,4,4-Trichloro-1,2-epoxybutane (b.p. 80-81°/25 mm.) was obtained from the Chemicals Division, Olin Mathieson Chemical Corp., and used as received.

3-(2-Propeneoxy)-1-amino-2-propanols. A mixture of 0.40 mole of the amine and 0.30 mole of allyl glycidyl ether was heated at 85° to 125° C. for 4 to 8 hours. A moderately exothermic reaction was usually observed. The reaction mixture was then cooled to room temperature and distilled under reduced pressure. The excess amine was recovered as the first fraction. The amino alcohols were obtained as the second fraction.

4,4,4-Trichloro-1-amino-2-butanol Hydrochlorides. To a well-stirred boiling solution of amine (0.22 mole) in 150 ml. of solvent (ethanol or toluene), 4,4,4-trichloro-1,2-epoxybutane (0.20 mole) was added dropwise over 1 to 2.5 hours. The reaction mixture was boiled under reflux for 2 to 7 hours. The solvent was removed in vacuo, and the residual oil was dissolved in 300 ml. of anhydrous ether. Ethereal hydrogen chloride was then added dropwise (ice bath) until precipitation was complete. The solid product was collected, washed with ether, and recrystallized from ethanol plus ethyl acetate.

ACKNOWLEDGMENT

The authors express their thanks to the Analytical Services Department of Olin for the analytical determinations.

LITERATURE CITED

(1) Bruson, H.A. (to Industrial Rayon Corp.), U.S. Patent **2,712,015** (June 28, 1955).
(2) Ladd, E.C., Harvey, M.P. (to Dominion Rubber Co.,), Can. Patent **527,462** (July 10, 1956).

RECEIVED for review December 4, 1967. Accepted June 17, 1968. Material supplementary to this article has been deposited as Document No. 10058 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and by remitting $1.25 for photoprints or $1.25 for 35-mm. microfilm. Advance payment is required. Make checks or money orders payable to Chief, Photoduplication Service, Library of Congress.

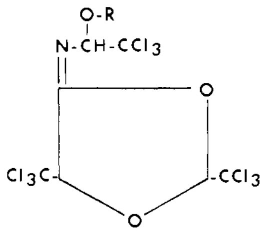
Esters of 2,5-Bis(trichloromethyl)-*N*-(1-hydroxy-2,2,2-trichloroethyl)-4-imino-1,3-dioxolane

GEORGE G. KING, J. V. KARABINOS, and HEINZ J. DIETRICH
Olin Research Center, New Haven, Conn. 06504

Esters of 2,5-bis(trichloromethyl)-*N*-(1-hydroxy-2,2,2-trichloroethyl)-4-imino-1,3-dioxolane, Wallach's compound, were synthesized.

THE SYNTHESIS of Wallach's compound from chloral or chloral hydrate and potassium cyanide (*2, 3, 6*) and the preparation of its acetate, benzoate, and ethylcarbonate ester derivatives have been described (*1, 3, 4*).

Recently, Franck and Hennessy (*4*) reported the structure of Wallach's compound to be 2,5-bis(trichloromethyl)-*N*-(1-hydroxy-2,2,2-trichloroethyl)-4-imino-1,3-dioxolane (I, R = H). Their conclusion was based on the chemical behavior and infrared and NMR spectra of Wallach's compound and its benzoate ester (I, R = C_6H_5CO).


I

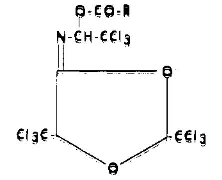
We have synthesized nine new esters of 2,5-bis(trichloromethyl)-*N*-(1-hydroxy-2,2,2-trichloroethyl)-4-imino-1,3-dioxolane. The physical properties of these compounds are summarized in Table I.

The infrared spectra of these esters had two strong absorption bands in the 5.5- to 6-micron region. The first band at 5.60 to 5.70 microns was assigned to the carbonyl group of the ester. This band position is similar to that observed for the carbonyl group in esters of chloral hemimercaptals, R—S—$CH(O_2CR)CCl_3$ (*5*). The second strong absorption band appeared at 5.75 to 5.80 microns and was assigned to the iminocarbonyl group. Franck and Hennessy (*4*) have reported that Wallach's compound had an infrared absorption band at 1745 cm.$^{-1}$ due to the iminocarbonyl group, and that its benzoate ester had a broad infrared absorption at 1750 to 1730 cm.$^{-1}$

EXPERIMENTAL

The infrared spectra were recorded on Perkin-Elmer Model 137 infrared spectrophotometer in KBr disks. The

Table I. Characterization of Esters of 2,5-Bis(trichloromethyl)-N-(1-hydroxy-2,2,2-trichloroethyl)-4-imino-1,3-dioxolane



Compound No.	R	M.P., °C[a]	Yield, %[b]	Molecular Formula	Analytical Data: Nitrogen, % Calcd.	Nitrogen, % Found	Chlorine, % Calcd.	Chlorine, % Found
1	$ClCH_2$-	134-36	47	$C_9H_5Cl_{10}NO_4$	2.57	2.69	65.0	64.7
2	C_2H_5-	154-56	60	$C_{10}H_8Cl_9NO_4$	2.67	2.85	60.8	60.6
3	n-C_3H_7	103-07	61	$C_{11}H_{10}Cl_9NO_4$	2.60	2.79	59.2	59.0
4	$Cl(CH_2)_2$-	121-24	33	$C_{10}H_7Cl_{10}NO_4$	2.50	2.66	63.4	63.4
5	2-ClC_6H_4-	135-36	70	$C_{14}H_7Cl_{10}NO_4$	2.31	2.34	58.3	58.2
6	4-ClC_6H_4-	152-58	71	$C_{14}H_7Cl_{10}NO_4$	2.31	2.44	58.3	58.0
7	C_2H_5S	137-40	35	$C_{10}H_8Cl_9NO_4S$[c]	2.51	2.73	57.3	57.3
8	n-C_3H_7S	105-07	31	$C_{11}H_{10}Cl_9NO_4S$[d]	2.45	2.71	55.8	55.7
9	C_6H_5S	142-44	35	$C_{14}H_8Cl_9NO_4S$[e]	2.31	2.58	52.7	52.8

[a] Melting points for analytical samples. [b] Yields for once or twice recrystallized products. [c] Calcd. for sulfur, 5.75; found, 5.58. [d] Calcd. for sulfur, 5.61; found, 5.46. [e] Calcd. for sulfur, 5.30; found, 5.10.

melting points were determined in capillary tubes with a Mel-Temp capillary melting point apparatus.

General Procedure. To a well stirred solution of 20.0 grams (0.043 mole)of 2,5-bis(trichloromethyl)-*N*-(1-hydroxy-2,2,2-trichloroethyl)-4-imino-1,3-dioxolane (*2*, *3*, *6*) and 15 ml. of pyridine in 125 ml. of toluene at 5° C. (ice bath), an acyl halide (0.050 mole) was added dropwise. The reaction mixture was allowed to warm to room temperature. After stirring for 2½ to 6 hours at room temperature, the reaction mixture was poured into 250 ml. of cold water. The toluene layer was separated, washed with an additional 250 ml. of water, and dried over anhydrous magnesium sulfate. The drying agent was removed by filtration, and the filtrate was evaporated. The resulting solid residue was recrystallized from ethanol.

ACKNOWLEDGMENT

The authors express their thanks to the Analytical Services Department of Olin for the analytical determinations.

LITERATURE CITED

(1) Bowman, R.E., Campbell, A., Tanner, E.M., *J. Chem. Soc.* 1963, 692.
(2) Cech, C.O., *Ber.* 9, 1020 (1876).
(3) Crowther, H.L., McCombie, H., Reade, T.H., *J. Chem. Soc.* 1914, 933.
(4) Franck, R.W., Hennessy, D.J., *J. Org. Chem.* 30, 1670 (1965).
(5) King, G.G., unpublished results.
(6) Wallach, O., *Ann. Chem.* 173, 297 (1874).

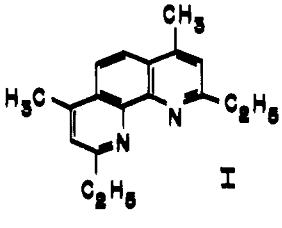
RECEIVED for review December 4, 1967. Accepted May 20, 1968.

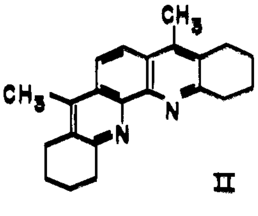
Synthesis of Certain Polyalkyl Quinolines and 1,10-Phenanthrolines

K. C. JOHN and FRANCIS H. CASE
Chemistry Department, Temple University, Philadelphia, Pa., 19122

The preparation of 2,9-diethyl-4,7-dimethyl- and of 2,3,8,9,-dicyclohexeno-4,7,dimethyl-1,10-phenanthrolines and of 3,6,8-trimethyl-, 2-ethyl-3,6,8-trimethyl-, and 3-ethyl-6,8-dimethyl-2-*n*-propylquinolines is described.

ATTEMPTS were made to synthesize 1,10-phenanthrolines substituted in the 2,9-positions by ethyl or *n*-propyl groups for possible use in chelating Cu(I). For this purpose modified Skraup (*1*) reactions were carried out using the following α,β-unsaturated aldehydes or ketones in presence of *o*-nitroaniline: 2-methyl-2-pentenal (*2*), 2-ethyl-2-hexenal (*2*), 3-hepten-2-one (*3*), 3-hexen-2-one (*4*), and 1-acetylcyclohexene (*5*). Only in the two last mentioned cases was the reaction successful. Reduction of the resulting 8-nitroquinoline to the amine followed by a second Skraup reaction using the same reagent produced the desired substituted 1,10-phenanthrolines, 2,9-diethyl-4,7-dimethyl- (I) and 2,3,8,9-dicyclohexeno-4,7-dimethyl-1,10-phenanthroline (II).





Use of 8-aminoquinoline in a Skraup reaction with 1-acetylcyclohexene yielded 2,3-cyclohexeno-4-methyl-1,10-phenanthroline.

In the case of 3-hepten-2-one, although it could not be caused to react with *o*-nitroaniline, it did yield the expected