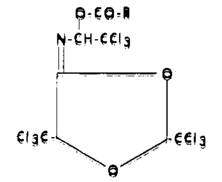
Table I. Characterization of Esters of 2,5-Bis(trichloromethyl)-N-(1-hydroxy-2,2,2-trichloroethyl)-4-imino-1,3-dioxolane



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

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Synthesis of Certain Polyalkyl Quinolines and 1,10-Phenanthrolines

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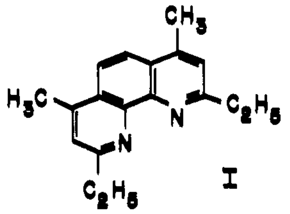
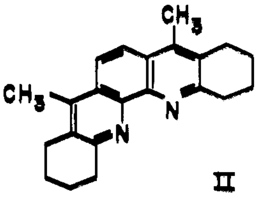
The preparation of 2,9-diethyl-4,7-dimethyl- and of 2,3,8,9,-dicyclohexeno-4,7,dimethyl-1,10-phenanthrolines and of 3,6,8-trimethyl-, 2-ethyl-3,6,8-trimethyl-, and 3-ethyl-6,8-dimethyl-2-n-propylquinolines is described.

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).


I


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

4,6-dimethyl-2-*n*-propyl-8-nitroquinoline when treated with 4-methyl-2-nitroaniline. This was reduced to the amine, but no phenanthroline could be obtained on subsequent treatment with the unsaturated ketone.

New polyalkyl quinolines (Table I) were obtained by treating 2,4-dimethylaniline in Skraup reactions with α-methylacrolein, 2-methyl-2-pentenal, and 2-ethyl-2-hexenal.

EXPERIMENTAL

General Procedure for the Synthesis of Polyalkyl- and 8-Nitropolyalkylquinolines. A stirred mixture of 0.1 mole of the appropriate aniline or *o*-nitroaniline, 0.2 mole of arsenic acid, and 100 ml. of 85% phosphoric acid was heated to 100° C. and treated with 0.2 mole of the α,β-unsaturated aldehyde or ketone, keeping the temperature below 120° C. After the addition was complete, the temperature was maintained at 120° C. for a period of 2 hours. The reaction mixture was then cooled, poured on ice, and made alkaline with concentrated potassium hydroxide solution. The residue was filtered from the solution, and both the solution and residue were extracted with hot benzene. The benzene was removed by distillation, and the residue was further purified by crystallization from a suitable solvent in the case of solids or by distillation followed by chromatographic methods in the case of liquids (Tables I and II).

Preparation of 8-Aminoquinolines. To a stirred solution of 0.4 mole of stannous chloride dihydrate ($SnCl_2 \cdot 2H_2O$) in 400 ml. of concentrated hydrochloric acid cooled to 10° was added 0.1 mole of the appropriate 8-nitroquinoline dissolved in 120 ml. of concentrated hydrochloric acid. After the addition was completed, the mixture was stirred at 10° C. for 1 hour and then slowly brought to room temperature. It was then made alkaline with 40% sodium hy-

Table I. Polyalkyl Quinolines

Quinoline	1st Component Aniline	2nd Component	M.P./B.P., ° C.	Yield, %	Analyses			
					Calcd., %		Found,[a] %	
					C	H	C	H
3,6,8-Trimethyl-	2,4-Dimethyl-	α-Methyl acrolein	105–106[b] at 0.5 mm.	24	84.17	7.65	84.57	7.81
2-Ethyl-3,6,8-trimethyl-	2,4-Dimethyl-	2-Methyl-2-pentenal	61–62[c]	9	84.37	8.60	84.35	8.47
3-Ethyl-6,8-dimethyl-2-*n*-propyl-	2,4-Dimethyl-	2-Ethyl-2-hexenal	130–135[d] at 0.5 mm.	6	84.53	9.31	84.24	9.17

[a] Microanalyses were done by Micro-Tech Laboratories, Inc., Skokie, Ill. [b] Analytical sample was prepared by V.P.C. using 10% Apiezon L on Chromosorb 60/80 at 230–235° C. [c] Recrystallized from methanol. [d] Analytical sample was prepared by adsorption chromatography using an alumina column and petroleum ether as eluent.

Table II. 8-Nitroquinolines

8-Nitroquinoline	1st Component Aniline	2nd Component	M.P., ° C.	Yield, %	Analyses			
					Calcd., %		Found, %	
					C	H	C	H
2-Ethyl-4-methyl-	2-Nitro-	3-Hexen-2-one	68–69[a]	25	66.65	5.59	66.92	5.57
4,6-Dimethyl-2-*n*-propyl-	4-Methyl-2-nitro-	3-Hepten-2-one	91–92[a]	31	68.83	6.60	68.83	6.45
2,3-Cyclohexeno-4-methyl-	2-Nitro-	1-Acetylcyclohexene	173–174[b]	7	69.41	5.82	69.65	6.03

[a] Crystallized from petroleum ether. [b] Recrystallized from methanol.

Table III. 8-Aminoquinolines

8-Aminoquinoline	M.P./B.P., ° C.	Yield, %	Analyses				Infrared μ, NH_2
			Calcd., %		Found, %		
			C	H	C	H	
2-Ethyl-4-methyl-	68[a]	77	77.38	7.58	77.60	7.64	2.90; 3.02
4,6-Dimethyl-2-*n*-propyl-	140–143 at 0.5 mm.	81	78.46	8.47	78.46	8.54	2.89; 2.99
2,3-Cyclohexeno-4-methyl-	123[a]	72	79.21	7.60	78.74	7.57	2.87; 2.96

[a] Crystallized from petroleum ether.

Table IV. 1,10-Phenanthrolines

1,10-Phenanthroline	1st Component Quinoline	2nd Component	M.P., ° C.	Yield, %	Analyses			
					Calcd., %		Found, %	
					C	H	C	H
2,9-Diethyl-4,7-dimethyl-[a]	8-Amino-2-ethyl-4-methyl-	3-Hexen-2-one	84.5[b]	33	79.08	7.74	79.51	7.64
2,3-Cyclohexeno-4-methyl-	8-Amino-	1-Acetylcyclohexene	140–141[b]	7	82.25	6.45	82.28	6.28
2,3,8,9-Dicyclohexeno-4,7-dimethyl	8-Amino-2,3-cyclohexeno-4-methyl-	1-Acetylcyclohexene	250[c] (dec.)	12	79.01	7.84	78.51	7.51

[a] The analysis is for the hemihydrate, $C_{18}H_{20}N_2 \cdot \frac{1}{2}H_2O$; infrared spectrum shows absorption at 3.00 microns (NH) and 2.88 microns (OH). [b] Crystallized from petroleum ether. [c] Purified by elution with benzene–petroleum ether from an alumina column and further crystallization from the same solvent.

droxide, ice being added to keep the temperature below 20° C. The resulting precipitate was dissolved in ether and the ethereal solution dried over anhydrous sodium sulfate. After removal of the ether, the residue, if solid, was crystallized from petroleum ether or purified by fractional distillation at reduced pressure (Table III), if liquid.

Preparation of 1,10-Phenanthrolines. To a well-stirred mixture of 0.1 mole of the appropriate 8-aminoquinoline, 18 ml. of 80% arsenic acid, and 100 ml. of 87% phosphoric acid heated to 100°C., 0.2 mole of the α,β-unsaturated ketone was slowly added. Stirring was continued for 3 hours while the temperature was slowly raised to 130° C. The mixture was cooled, made alkaline with concentrated potassium hydroxide and the resulting precipitate removed by filtration. The filtrate and residue were extracted with hot benzene. After removal of benzene, the product was purified by crystallization from a suitable solvent (Table IV).

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1,3-Bis(o-hydroxybenzyl)-2-Substituted Imidazolidines

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Several 1,3-bis(o-hydroxybenzyl)-2-substituted imidazolidines were synthesized and characterized. Yields, melting points, and elemental analyses are reported for the new compounds.

USING THE PROCEDURE of Billman and Dorman (*1*) several 1,3-bis(*o*-hydroxybenzyl)-2-substituted imidazolidines were synthesized and tested for herbicidal activity.

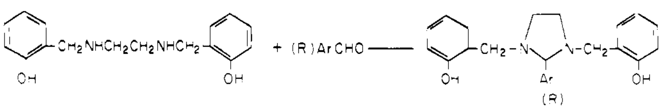


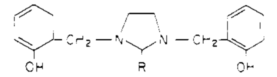
Table I summarizes yields, melting points, and elemental analyses of compounds prepared. A list of characteristic infrared absorption bands is shown in Table II. The infrared spectrum of each compound was consistent with the desired structure.

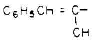
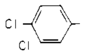
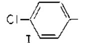
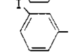
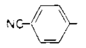
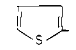
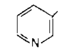
EXPERIMENTAL

N,N'-Bis(*o*-hydroxybenzyl)ethylenediamine was obtained from the Dow Chemical Co. Other reactants were also obtained comercially and used without further purification. Melting points were taken on a Hershberg melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer using potassium bromide as a matrix.

To a hot solution of *N,N'*-bis(*o*-hydroxybenzyl)ethylenediamine (0.1 mole) in 500 ml. of methanol was added 0.1 mole of the aldehyde dissolved in a minimum amount of methanol. The reaction mixture was refluxed for 1 hour

Table I. 1,3-Bis(o-hydroxybenzyl)-2-substituted Imidazolidines



Compound No.	Compound	R	% Yield	M.P., ° C.		Analyses % C	% H	% Cl	% N
1	1,3-Bis(*o*-hydroxybenzyl)-2-(α-methy-10-styryl)imidazolidine	 $C_6H_5CH{=}\underset{CH_3}{C}-$	80	115–16[a]	Calcd.	78.0	7.1	. . .	7.0
					Found	78.0	6.9		7.1
2	1,3-Bis(*o*-hydroxybenzyl)-2-*p*-chlorophenylimidazolidine		85	155–56[b]	Calcd.	70.0	5.9	9.0	7.1
					Found	70.0	5.8	8.9	7.1
3	2-(3,4-Dichlorophenyl)-1,3-bis(*o*-hydroxybenzyl)imidazolidine		88	106–07[a]	Calcd.	64.3	5.2	16.5	6.5
					Found	64.5	5.3	16.5	6.8
4	1,3-Bis(*o*-hydroxybenzyl)-2-*m*-iodophenylimidazolidine		87	138–39[b]	Calcd.	56.8[c]	4.8	. . .	5.8
					Found	57.0	4.8		5.7
5	2-(*p*-Cyanophenyl)-1,3-bis(*o*-hydroxybenzyl)imidazolidine		65	142–43[a]	Calcd.	74.8	6.0	. . .	10.9
					Found	74.6	6.1		10.8
6	1,3-Bis(*o*-hydroxybenzyl)-2-(2-thienyl)-imidazolidine		90	178–79[d]	Calcd.	68.8[e]	6.1	. . .	7.6
					Found	68.9	6.1		7.7
7	1,3-Bis(*o*-hydroxybenzyl)-2-(3-pyridyl)-imidazolidine		82	182–83[f]	Calcd.	73.1	6.4	. . .	11.6
					Found	73.0	6.4		11.8

[a] Recrystallized from methanol. [b] Recrystallized from 2-propanol. [c] Analyzed for iodine: Calcd. 26.1; found 25.8. [d] Recrystallized from pyridine. [e] Analyzed for sulfur: Calcd. 8.8; found 8.7. [f] Recrystallized from ethanol.

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