isopropyl alcohol, m.p. over 360°, and recrystallized from isopropyl alcohol–ether, m.p. over 360°.

Anal. Calcd. for $C_9H_{20}Cl_2N_2$: C, 47.58; H, 8.87; N, 12.33; Cl, 31.22. Found: C, 47.84; H, 8.85; N, 12.49; Cl, 31.30.

The picrate was formed in the usual manner in methanol, m.p. 236°, not changed on recrystallization.

Anal. Calcd. for $C_{21}H_{24}N_8O_{14}$: C, 41.16; H, 3.95. Found: C, 41.33; H, 4.21.

The *phenylurea* was formed from 0.5 g. of the amine and a slight excess of phenylisocyanate in benzene, m.p. 200–201°. On recrystallization from methanol, the m.p. was raised to 204°.

Anal. Calcd. for $C_{23}H_{28}N_4O_2$: C, 70.38; H, 7.19; N, 14.28. Found: C, 70.53; H, 7.44; N, 14.14.

The *phenylthiourea* was formed from 0.5 g. of the amine and phenylisothiocyanate in benzene, m.p. 185°. On recrystallization from methanol the m.p. was raised to 186°.

Anal. Calcd. for $C_{23}H_{28}N_4S_2$: C, 65.06; H, 6.65; N, 13.28. Found: C, 65.05; H, 6.90; N, 13.40.

The *dibenzamide* was formed from 0.5 g. of the amine and benzoyl chloride by the Schotten-Bauman procedure, m.p. 168–170°, increased to 170–170.5° on recrystallization from methanol.

Anal. Calcd. for $C_{23}H_{26}N_2O_2$: C, 76.21; H, 7.23; N, 7.73. Found: C, 76.24; H, 7.20; N, 7.83.

2,5-Bismorpholinoethylspiro[3.3]heptane dicarboxylate dihydrochloride (XVIIIc). The bismorpholinoethyl ester of Fecht acid was prepared by adding 4.42 g. (0.02 mole) of the acid chloride in 50 ml. of benzene to 5.24 g. (0.04 mole) of morpholinoethyl alcohol dissolved in 50 ml. of benzene and refluxing several hours. On cooling, the crude product crystallized. It was filtered, washed with benzene and ether, and dried, m.p. 199–201°, 8 g. (83%). Two recrystallizations from isopropyl alcohol–ether gave a constant melting product, m.p. 207–208°.

Anal. Calcd. for $C_{21}H_{36}Cl_2N_2O_6$: C, 52.17; H, 7.51; N, 5.80; Cl, 14.67. Found: C, 52.33; H, 7.66; N, 5.99; Cl, 14.70.

2,5-Bispiperidinoethylspiro[3.3]heptane dicarboxylate dihydrochloride (XVIIIb) was prepared in an analogous manner from 4.42 g. (0.02 mole) of the acid chloride and 5.17 g. (0.04 mole) of piperidinoethyl alcohol. There was obtained 7.8 g. (81%) of product which melted after two recrystallizations from isopropyl alcohol–ether, at 228–229°.

Anal. Calcd. for $C_{23}H_{40}Cl_2N_2O_4$: C, 57.60; H, 8.41; N, 5.84; Cl, 14.79. Found: C, 57.48; H, 8.76; N, 5.90; Cl, 14.97.

2,5-Bis(2-dimethylaminoethyl)spiro[3.3]heptane dicarboxylate dihydrochloride (XVIIIa) was prepared in an analogous manner from 6.63 g. (0.03 mole) of the acid chloride and 5.35 g. (0.06 mole) of 2-dimethylaminoethanol in 150 ml. of benzene and refluxed for 1 hr. There was obtained 11.55 g. crude product, m.p. 209–212° (94%). Recrystallization from methanol-ether raised the m.p. to 234–235° and from isopropyl alcohol–ethanol to 234.5–235°.

Anal. Calcd. for $C_{17}H_{32}Cl_2N_2O_4$: C, 51.13; H, 8.08; N, 7.02; Cl, 17.75. Found: C, 50.81; H, 8.02; N, 7.22; Cl, 17.60.

908 LINCOLN AVE.
FALLS CHURCH, VA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, KANSAS STATE COLLEGE AND STROSACKER'S LABORATORY, THE DOW CHEMICAL COMPANY]

Dichloromethylallyl Compounds. III. N-(3,3-Dichloro-2-methylallyl)amines

D. G. KUNDIGER,[1] H. PLEDGER, JR.,[2] AND R. L. SOULEN[3]

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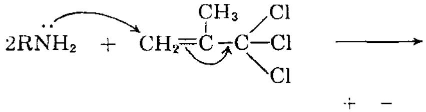
A new series of new amines were prepared by the reaction of 3,3,3-trichloro-2-methyl-1-propene and 1,1,3-trichloro-2-methyl-1-propene with *N*-substituted amines, ammonia, and hydrazine. The physical constants and the preparation of these compounds and some of their derivatives are reported.

In continuation of earlier studies[4] on the chemistry of 3,3,3-trichloro-2-methyl-1-propene (I) and 1,1,3-trichloro-2-methyl-1-propene (II) with nucleophilic reagents, this paper reports the results of a study of the reactions of these chlorides with *N*-substituted amines, ammonia, and hydrazines. Previous work[4,5] has indicated that these isomeric chlorides are highly reactive. The same compound results when either chloride reacts with the same nucleophile. For example, the reaction of aqueous sodium hydroxide with chloride I or II yields 3,3-dichloro-2-methyl-2-propen-1-ol.[6] The reactions of chlorides I and II with amino compounds has further substantiated the earlier indications. The highly exothermic reaction between amino compounds and chloride I probably proceeds by an SN2′ reaction.



$$2R\ddot{N}H_2 + CH_2{=}C(CH_3){-}CCl_3 \longrightarrow$$

$$RNHCH_2C(CH_3){=}CCl_2 + R\overset{+}{N}H_3\overset{-}{Cl} \qquad SN2'$$

The expected inductive withdrawal of electrons from nitrogen by the γ-chlorine atoms in the dichloromethylallyl group is greatly facilitated by the double bond in the allylic system. This base weakening effect leads to interesting results. This

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(1) Deceased.

(2) Present address, Organic Process Development Laboratory, The Dow Chemical Company, Freeport, Tex. To whom requests for reprints should be sent.

(3) Portions of this paper represent part of a dissertation submitted by Robert L. Soulen in partial fulfillment of the requirements for the Ph.D. degree at Kansas State University.

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(5) P. B. De La Mare and C. A. Vernon, *J. Chem. Soc.*, 3628 (1952)

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effect is strikingly demonstrated by *N*,*N*-bis(3,3-dichloro-2-methylallyl)aniline and by tris(3,3-dichloro-2-methylallyl)amine. Neither compound is soluble in concentrated hydrochloric acid but dissolves slowly in concentrated sulfuric acid. Dilution of the sulfuric acid solution yields the amine unchanged. During the reaction of *N*-(3,3-dichloro-2-methylallyl)aniline with chloride I under thermally forced conditions to produce *N*,*N*-bis(3,3-dichloro-2-methylallyl)aniline, gaseous hydrogen chloride was evolved. These forcing conditions illustrate the base weakening effect of one dichloromethylallyl group attached to nitrogen and the evolution of hydrogen chloride illustrates the even more pronounced effect of two such groups on nitrogen.

Whenever chloride I or II reacts with a primary amine there is a possibility of substitution of two additional groups. Again, however, because of the base weakening effect of one dichloromethylallyl group, substitution of one group predominates and is often exclusive. The predominance of substitution of one group is indicated by the reaction of aniline. Chloride I gave 52.5% monosubstituted aniline and 4.9% disubstituted aniline even though the reaction temperature exceeded 200°.

The reaction of chloride II and ammonia or hydrazine gave unstable products when only one or two dichloromethylallyl groups were substituted. Product stability increased with increase in the number of dichloromethylallyl groups attached to nitrogen. Rapid decomposition of (3,3-dichloro-2-methylallyl)amine and of bis(3,3-dichloro-2-methylallyl)hydrazine could be prevented by formation of the hydrochloride salt.

Pyridine reacted with either chloride I or II yielding the same compound in 100% yield. We have never established whether the compound is 2-(3,3-dichloro-2-methylallyl)pyridine hydrochloride or *N*-(3,3-dichloro-2-methylallyl)pyridinium chloride. We favor the latter structure, as it is the salt one would expect from the reaction scheme we have proposed.

The structure of the disubstituted hydrazine derived from hydrazine and chloride II is suspected of being *N*,*N'*-bis(2,2-dichloro-3-methylallyl)hydrazine, as the base weakening effect of the firstly substituted group should render the substituted nitrogen less basic than the unsubstituted nitrogen.

Table I contains physical constants of an analytical results on the various amines prepared in this work. Further evidence for their structure was obtained from their infrared absorption spectra. All showed strong absorption at 6.15–6.20 μ and at 11.10–11.22 μ typical of the $Cl_2C{=}C(CH_3)CH_2$— group.

EXPERIMENTAL

General method for the synthesis of N-(3,3-dichloro-2-methylallyl)amines. Either 3,3,3-trichloro-2-methyl-1-propene (I) or 1,1,3-trichloro-2-methyl-1-propene (II) was added slowly to the amine (2 moles of amine to 1 mole of chloride I or II). In most cases the reaction was exothermic and rapid but occasionally heating was required for initiation. After addition, the reaction mixture was heated for an additional period to insure complete reaction. Ether was added to the cooled mixture and the by-product amine hydrochloride separated in near quantitative or quantitative yields. Fractionation of the ether solution gave the *N*-(3,3-dichloro-2-methylallyl)amine. Physical constants and analyses of the various dichloromethylallylamines are listed in Table I.

N,N-Bis(3,3-dichloro-2-methylallyl)aniline. *N*-(3,3-Dichloro-2-methylallyl)aniline, 266.6 g. (1.23 moles), and 196.5 g. (1.23 moles) of 3,3,3-trichloro-2-methyl-1-propene were mixed and heated between 177–183° for 30 min., evolving hydrogen chloride rapidly. After standing 3 days the mixture solidified. This solid was stirred with ether and 10% sodium hydroxide solution. The base extracted ether was dried and concentrated to a solid which was recrystallized from absolute ethanol. The crystals (305.4 g.), m.p. 67.5–68.0°, were distilled giving a center cut, 205.8 g., b.p. 134° (0.4 mm.) –155° (0.2 mm.), m.p. 78.5–82.0°. This material was crystallized from 95% ethanol yielding 160.0 g. of pure *N*,*N*-bis(3,3-dichloro-2-methylallyl)aniline, m.p. 84.0–85.5°. A mixture melting point of this material with by-product *N*,*N*-bis(3,3-dichloro-2-methylallyl)aniline obtained from reaction of chloride I and aniline gave no depression. The infrared spectrum of this compound showed bands at 13.40 and 14.43 μ (typical of *N*,*N*-dialkylated-aniline), 6.15 and 11.21 μ (typical of $Cl_2C{=}C(CH_3)CH_2$— and no band at 2.93 μ (typical of N—H). Analyses are in Table I.

N-(3,3-Dichloro-2-methylallyl)pyridinium chloride. One mole (79.0 g.) of pyridine and 159.5 g. (1.0 mole) of 3,3,3-trichloro-2-methyl-1-propene were mixed and slowly heated to 120° with gradual separation of a red oil. Without further heating, the temperature rapidly rose to 143°. Upon cooling small amounts of ether were added that induced crystallization. The solid was broken up, added to boiling dry carbon tetrachloride, filtered, and dried *in vacuo*. The resulting brown solid (234 g., 99%), m.p. 148.5–150.0°, was used for analysis.

Anal. Calcd. for $C_9H_{10}Cl_3N$: C, 45.32; H, 4.19. Found: C, 45.62; H, 4.09.

The solid was very hygroscopic, dissolved in ethanol and water, and gave an immediate precipitate with aqueous silver nitrate.

3,3-Dichloro-2-methylallylamines. Procedure I. Ammonia was bubbled into a mixture of 478.2 g. (3.0 moles) of 1,1,3-trichloro-2-methyl-1-propene in 500 ml. of 95% ethanol for 3.5 hr. The temperature was held below 35° by a cooling bath during addition, then allowed to stand 2 hr. at room temperature. Hydrogen chloride was bubbled into the alcohol solution until acid to litmus. The solution was concentrated under reduced pressure, ether added, and the amine hydrochlorides filtered. Distillation of the ether gave 21.5 g. of unchanged starting halide and a solid residue. Recrystallization of this solid from ethanol gave 74 g. (17%) of tris(3,3-dichloro-2-methylallyl)amine, m.p. 63.5–65.0°. Analyses are in Table I.

The amine hydrochlorides were mixed into excess 10% sodium hydroxide and extracted with ether. The combined ether extracts were dried and distilled to give 6.6 g. (2.7%) of 3,3-dichloro-2-methylallylamine, b.p. 33° (0.9 mm.), n_D^{20} 1.5052 and 149.6 g. (27%) of bis(3,3-dichloro-2-methylallyl)amine, b.p. 103° (0.3 mm.), n_D^{20} 1.5245.

The primary amine was unstable and decomposed rapidly at room temperature. The hydrochloride salt, m.p. 201–202°, was stable. Analyses are in Table I.

The secondary amine hydrochloride, m.p. 157–158°, was stable and the free amine decomposed after prolonged periods. Analyses are in Table I.

Procedure II. Anhydrous methanol (200 ml.) and 209 g. (1.31 moles) of 1,1,3-trichloro-2-methyl-1-propene were added to approximately 50 ml. of liquid ammonia cooled

TABLE I

PROPERTIES OF SUBSTITUTED DICHLOROMETHYLALLYL AMINES, $Cl_2C{=}C(CH_3){-}CH_2{-}N(R)(R')$

Halide Used[a]	R	R′	B.P.	Mm.	n_D^{20}	d_4^{20}	Carbon, %		Hydrogen, %		Chlorine, %		Yield, %
							Calcd.	Found	Calcd.	Found	Calcd.	Found	
I	Phenyl	H	111–112	0.9	1.5841	1.243	55.58	55.26	5.13	5.15	32.82	32.45	52.5
I	Phenyl	$Cl_2C{=}C(CH_3)CH_2{-}$	83.5–84.5[b]	—	—	—	49.7	49.4	4.46	4.37	41.82	42.45	4.9[c]
II	Phenyl	H	111–112	0.5	1.5831	—	—	—	—	—	—	—	79.9
I	Phenyl	Methyl	95	0.1	1.5768	1.208	—	—	—	—	30.8	32.1	58.8
I[e]	Phenyl	$Cl_2C{=}C(CH_3)CH_2{-}$	84.5–85.5[b]	—	—	—	—	—	—	—	—	—	48.2
II	Cyclohexyl	H	83	0.6	1.4757	1.104	54.4	53.54	7.31	8.22	—	—	69.8
II	Cyclohexyl	H	not dist.	—	1.4760	—	—	—	—	—	—	—	80.1
I	*n*-Butyl	*n*-Butyl	71–73	0.2	1.4709	0.996	57.14	57.17	9.15	8.70	—	—	72.5
II	*n*-Butyl	*n*-Butyl	not dist.	—	1.4693	—	—	—	—	—	—	—	99.0
II	*n*-Butyl	H	64	1.0	1.4756	1.053	49.0	50.3	8.05	7.72	—	—	52.0
I	1,1,3,3-Tetramethylbutyl	H	78	0.5	1.4788	1.061	57.2	57.0	9.15	8.81	28.1	28.3	59.2
I	*N*(R)(R′)=Piperidyl	—	56	0.1	1.5000	1.103	51.9	52.2	7.27	7.23	—	—	77.0
I	*N*(R)(R′)=Morpholyl	—	72.5	0.8	1.5010	1.187	45.7	45.9	6.24	6.42	—	—	76.0
II	2-Aminoethyl	H	76	1.0	1.5088	1.183	39.4	39.2	6.62	6.57	38.8	38.1	35.4
II	2-Hydroxyethyl	H	107.5	2.2	1.5110	1.225	39.2	39.4	6.03	6.28	38.5	37.9	21.9
II	2-Hydroxyethyl	$Cl_2C{=}C(CH_3)CH_2{-}$	145	0.9	1.5283	—	39.4	39.3	4.93	5.25	46.	45.6	32.7
I[e]	H	H	38	1.1	1.5048	—	—	—	7.36[d]	7.78[d]	60.25	59.98	11.2
I	$Cl_2C{=}C(CH_3)CH_2{-}$	H	96	0.2	1.5242	—	—	—	5.33[d]	5.28[d]	53.90	53.65	68.7
I	$Cl_2C{=}C(CH_3)CH_2{-}$	$Cl_2C{=}C(CH_3)CH_2{-}$	63.5–65.0[b]	—	—	—	—	—	3.64[d]	3.41[d]	55.11	55.35	17.0
I	N(R)(R′)=phthalimidyl	—	118–119[b]	—	—	—	—	—	—	—	26.28	26.47	79.0
I	$Cl_2C{=}C(CH_3)CH_2NH{-}$	$Cl_2C{=}C(CH_3)CH_2{-}$	90–91[b]	—	—	—	—	—	6.98[d]	6.64[d]	53.15	53.36	31.0
I[e]	$Cl_2C{=}C(CH_3)CH_2NH{-}$	H	112	0.2	—	—	30.55	30.75	8.91[d]	9.15[d]	56.47	56.04	37.0

[a] I is 3,3,3-trichloro-2-methyl-1-propene. II is 1,1,3-trichloro-2-methyl-1-propene. [b] Melting point. [c] Equimolar quantities of halide and *N*(3,3-dichloro-2-methylallyl)aniline. [d] Nitrogen analysis. [e] Analysis on hydrochloride salt.

by a Dry Ice bath. A slow stream of ammonia was bubbled through the mixture for 24 hr. as it warmed to room temperature. The reaction mixture was concentrated under reduced pressure, poured into 300 ml. of 20% sodium hydroxide, and extracted repeatedly with ether. The ether was dried, treated with hydrogen chloride, and the amine hydrochlorides removed. The ether gave 7.5 g. of starting chloride. The amine hydrochlorides were converted to the free amines and distilled to give 19.8 g. (11%) of 3,3-dichloro-2-methylallylamine, b.p. 38° at 1.1 mm. and 114.3 g. (69%) of bis-(3,3-dichloro-2-methylallyl)amine, b.p. 97° at 0.2 mm.

The benzenesulfonamide of the primary amine was recrystallized from ethanol, m.p. 72–74°. Reported value[7] is m.p. 72–74°.

The acetamide of the secondary amide was prepared from acetic anhydride and bis(3,3-dichloro-2-methylallyl)amine and distilled at 129° (0.01 mm.), n_D^{20} 1.5344.

The dichloroacetamide of the secondary amine was prepared from dichloroacetyl chloride and bis(3,3-dichloro-2-methylallyl)amine and was recrystallized from petroleum ether (b.p. 60–70°) to give a white solid, m.p. 100.0–102.5°.

The trichloroacetamide of the secondary amine was prepared from trichloroacetyl chloride and bis(3,3-dichloro-2-methylallyl)amine and was recrystallized from ethanol to give a slightly yellow solid, m.p. 56.0–58.5°.

The benzenesulfonamide of the secondary amine was crystallized from ethanol, m.p. 131–132°.

3,3-Dichloro-2-methylallylamine via Gabriel synthesis. The Sheehan and Bolhofer modification[8] of the Gabriel synthesis was used to prepare *N*-(3,3-dichloro-2-methylallyl)-phthalimide. From 190 g. (1.02 moles) of potassium phthalimide and 159.4 g. (1.0 mole) of 1,1,3-trichloro-2-methyl-1-propene was obtained 214 g. (79%) of *N*-(3,3-dichloro-2-methylallyl)phthalimide, m.p. 118–119°. Analyses are in Table I.

The Ing and Manske modification[9] of the Gabriel synthesis was used for the hydrolysis of *N*-(3,3-dichloro-2-methylallyl)phthalimide. From 54 g. (0.2 mole) of the phthalimide was obtained 17.2 g. (61%) of 3,3-dichloro-2-methylallylamine, b.p. 85–87° (50 mm.), n_D^{29} 1.4992.

Bis and tris(3,3-dichloro-2-methylallyl)hydrazine. To 320 g. (2.0 moles) of 1,1,3-trichloro-2-methyl-1-propene in 400 ml. ethanol was added 110 g. (3.44 moles) of anhydrous hydrazine in small portions during 1 hr. The reaction was heated at 60° for an additional hour. After cooling, the solid was separated and identified as hydrazine hydrochloride, m.p. 87–89°. The alcohol solution was concentrated under reduced pressure and poured into 5% hydrochloric acid. The solid which separated was washed with 4500 ml. of hot water and was crystallized from ethanol. The solid was identified as tris(3,3-dichloro-2-methylallyl) hydrazine, m.p. 90–91°. Analyses are in Table I.

The hot water washes and the acid solution were combined, made basic with sodium hydroxide, and extracted repeatedly with ether. The ether was dried and distilled to give 101.8 g. (37%) of bis(3,3-dichloro-2-methylallyl hydrazine, b.p. 109–115° (0.2 mm.) and an undistilled solid in the distilling flask. The distillate decomposed rapidly to resinous products but was stable as the hydrochloride salt, m.p. 143–145°. Analyses are in Table I.

This compound was believed to be the symmetrical isomer (see discussion).

The undistilled portion was dissolved in boiling petroleum ether (b.p. 60–70°) and on cooling gave two crystalline forms. These crystals were hand separated: 29.0 g. of hard square plates, m.p. 88°, identical with the tris(3,3-dichloro-2-methylallyl)hydrazine isolated above; 24.0 g. of soft fine needles which were tris(3,3-dichloro-2-methylallyl)hydrazine hydrochloride, m.p. 164–165°. Total yield of the trisubstituted hydrazine was 31%.

Anal. Calcd. for $C_{12}H_{17}Cl_7N_2$: Cl^- 8.11; Cl, 56.75; N, 6.41. Found: Cl, 8.06; Cl, 56.37; N, 6.21.

Acknowledgment. We wish to express our gratitude to The Dow Chemical Company for their financial support of this research.

MIDLAND, MICH.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Allylic Chlorides. XXVI. The 1-Chloro-2-heptenes and 1-Chloro-4,4-dimethyl-2-pentenes

LEWIS F. HATCH, HERBERT D. WEISS,[1] AND TAO PING LI

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The 1-chloro-2-heptenes and the 1-chloro-4,4-dimethyl-2-pentenes have been synthesized, characterized, and their relative reactivities toward potassium iodide in acetone and sodium ethoxide in ethanol determined. The data indicate that the rate of reaction is influenced more by the steric requirements imposed by the nature of the group in the *gamma* position of allyl chloride than by inductive effects. Energies and entropies of activation have been calculated for the reaction of the 1-chloro-4,4-dimethyl-2-pentenes with both of these reagents.

The relative reactivities of various methyl substituted allylic chlorides toward potassium iodide in acetone and sodium ethoxide in ethanol have been reviewed by Hatch and Noyes.[2] This area of research has now been extended to include the 1-chloro-2-heptenes (γ-*n*-butylallyl chlorides) and the 1-chloro-4,4-dimethyl-2-pentenes (γ-*tert*-butylallyl chlorides) in order to evaluate further the influence of steric factors on these reactions. A similar study has been made by Bartlett and Rosen on the effect of *n*-butyl and *t*-butyl groups for the reaction between potassium iodide in ace-

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[1] Present address: American Alcolac Corporation, Baltimore 26, Md.

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