overnight at room temperature, concentrated to about 120 ml. under reduced pressure and added to 50 ml. of water. The solution was adjusted to *p*H 7 with hydrochloric acid and extracted with ether. The extracts were washed with water, dried over magnesium sulfate and concentrated. The residue was the impure hydroxy ester, a mixture of an oil and a crystalline solid which melted at 118–119.2° after crystallization from aqueous acetone, but was not analytically pure. A solution of 1.6 g. of the crude hydroxy ester (the oil described above) in 25 ml. of dry benzene was treated with 1.0 g. of phosphorus pentoxide at room temperature for 15 minutes with intermittent shaking, which was continued for 2 hr. longer after addition of another 1.0-g. portion of phosphorus pentoxide. The organic layer was removed by decantation, and the solid residue was treated with water (50 ml.) and extracted with ether and then with benzene. The organic extracts were combined, washed with water and dried over magnesium sulfate. Removal of the solvents under reduced pressure gave a light yellow oil which on trituration with cold ether gave a white solid (100 mg., 7%), m.p. 267–269.2°, which was removed by filtration. Recrystallization from acetonitrile gave an analytical sample, m.p. 268.5–269.3°, of a by-product of unknown structure which is an isomer of the normal dehydration product described below.

Anal. Calcd. for $C_{15}H_{12}O_2$: C, 80.33; H, 5.44. Found: C, 80.14; H, 5.62.

The filtrate remaining after removal of the above compound was concentrated and the residue sublimed at 100–140° (0.3 mm.). The white sublimate amounted to 550 mg. (42%) of XVI, m.p. 126.9–127.7°. Recrystallization from ether yielded an analytical sample, m.p. 127.8–128.4°, as fine white needles.

Anal. Calcd. for $C_{15}H_{12}O_2$: C, 80.33; H, 5.44. Found: C, 80.09; H, 5.56.

A solution of 100 mg. of the ester XVI in 20 ml. of ethyl acetate was hydrogenated in the presence of 30 mg. of 10% palladium-on-Norit at room temperature. Hydrogen absorption amounted to 91% of one molar equivalent in 50 minutes. The product XVII was purified by crystallization from 30–60° petroleum ether with cooling in Dry Ice and amounted to 92 mg. (92%). The ester formed clusters of white needles, m.p. and mixed m.p. with an authentic sample of XVII described below, 34.1–35°.

Methyl 2,3-Dihydro-1H-benz(*e*)indene-3-carboxylate (XVII).—2,3-Dihydro-1H-benz(*e*)indene-3-carboxylic acid[14] was esterified with methanol in the presence of *p*-toluenesulfonic acid. The ester XVII was obtained in 81% yield after crystallization from 30–60° petroleum ether. An analytical sample had m.p. 34.6–34.8°.

Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.62; H, 6.23. Found: C, 79.46; H, 6.17.

Michael Addition of Dimethyl Malonate to Methyl 1H-benz(*e*)indene-3-carboxylate (XVI).—To a solution of sodium methoxide prepared from sodium (0.093 g.) and 25 ml. of anhydrous methanol was added a solution of dimethyl malonate (2.5 g.) in anhydrous methanol (25 ml.). A solution of methyl 1H-benz(*e*)indene-3-carboxylate (0.90 g.) in a mixture of dry toluene (90 ml.) and anhydrous methanol (10 ml.) was added rapidly with stirring. After the reaction mixture had been heated under reflux for 16 hr., it was cooled and glacial acetic acid (5 ml.) was added. The mixture was dissolved in ether, and the solution was washed with sodium bicarbonate solution, water and dried over magnesium sulfate. Removal of the solvent gave a dark colored oil (0.9 g.) which was subjected to a short-path distillation under reduced pressure. The unreacted starting material XVI (380 mg.) sublimed first and was removed. A pale yellow very viscous oil distilled at 200–230° (0.1 mm.) (442 mg., 53% of the slightly impure ester XVIII, based on the amount of methyl 1H-benz(*e*)indene-3-carboxylate that was not recovered).

Anal. Calcd. for $C_{20}H_{20}O_6$: C, 67.44; H, 5.66. Found: C, 68.06; H, 5.76.

3-Carboxy-2,3-dihydro-1H-benz(*e*)indene-2-acetic Acid (III).—One hundred and eighty milligrams of the tricarboxylic acid ester described above was heated under reflux for 33 hr. with 20 ml. of 5% potassium hydroxide in 1:3 aqueous methanol. Removal of the methanol, followed by acidification with hydrochloric acid, precipitated a brown solid. An equal volume of concentrated hydrochloric acid was added, followed by glacial acetic acid (5 ml.), and the suspension was heated under reflux for 4 hr. The solution was separated from some dark undissolved material by decantation through glass wool, and the filtrate was allowed to stand overnight at 5°. A light brown solid was obtained (82 mg., 65%), m.p. 232.6–233.6°. Two recrystallizations from acetonitrile gave white crystals of III, m.p. 234.5–235.1°. A mixture of this acid with III obtained by saponification of the thermal rearrangement product of diethyl α-allyl-2-naphthalenemalonate (m.p. 234.5–235.2°) melted at 234.7–235.2°. The infrared spectra of samples of the acid from both sources were identical. The acid prepared by this method on treatment with acetic anhydride by the procedure described above formed the anhydride IV, identical with a sample of IV derived from the rearrangement product II.

CAMBRIDGE, MASSACHUSETTS

(14) W. H. Linnell, D. W. Mathieson and D. T. Modi, *J. Chem. Soc.*, 3257 (1953).

[CONTRIBUTION FROM THE ORGANIC CHEMICALS DIVISION, ST. LOUIS RESEARCH DEPARTMENT, MONSANTO CHEMICAL CO.]

Preparation of Some New 2-Chloroacetamides

BY A. J. SPEZIALE AND P. C. HAMM

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The synthesis of some new N-substituted 2-chloroacetamides and 2′-chloroacetanilides is described. Some new intermediates used in the preparation of this new class of herbicides are also presented.

A study of the phytotoxicity of N-substituted 2-chloroacetamides has shown that many of them possess outstanding effectiveness and selectivity for the control of annual grasses.[1] The synthesis of those 2-chloroacetamides and intermediates which were prepared during the course of this study but not previously reported is presented here.

The 2-chloroacetamides listed in Table I were prepared from the appropriate amine and chloroacetyl chloride by the method given for N-butyl-2-chloroacetamide. Slight modifications of this method were used depending on the nature of amine and final product. Where the amine hydrochloride was available, it was used directly, the quantity of sodium hydroxide being altered accordingly.

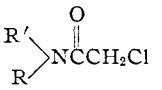
The 2-chloroacetanilides bearing negative groups were prepared by the method of Jacobs and Heidelberger[2] or by refluxing equimolar amounts of the aniline derivative and chloroacetyl chloride in dry benzene. This latter method is described for 2,2′-dichloro-4-nitroacetanilide.

(1) P. C. Hamm and A. J. Speziale, 127th Meeting, American Chemical Society, Cincinnati, Ohio, March 30–April 2, 1955.

(2) W. A. Jacobs and M. Heidelberger, THIS JOURNAL, **39**, 1439 (1917).

TABLE I

N-SUBSTITUTED-2-CHLOROACETAMIDES



R	R′	Yield, %	M.p., °C.	B.p. 0°C.	B.p. Mm.	$n^{25}D$	Formula	Chlorine, % Calcd.	Chlorine, % Found
n-C_3H_7	n-C_3H_7	88	.....	120	8.0	1.4670	$C_8H_{16}ClNO$	19.96	20.13
H	i-C_3H_7	88	62–62.5	..	..	....	$C_5H_{10}ClNO$	26.15	26.33
i-C_3H_7	i-C_3H_7	52	48.5–49.5	86	2.7	1.4619[a]	$C_8H_{16}ClNO$	19.96	20.05
H	n-C_4H_9	93	.....	110	7.0	1.4665	$C_6H_{12}ClNO$	23.69	24.14
C_2H_5	n-C_4H_9	93	.....	90	1.5	1.4665	$C_8H_{16}ClNO$	19.96	20.58
i-C_3H_7	n-C_4H_9	73	.....	82	0.5	1.4655	$C_9H_{18}ClNO$	18.49	18.59
n-C_4H_9	n-C_4H_9	94	.....	92	0.2	1.4661	$C_{10}H_{20}ClNO$	17.24	17.64
i-C_4H_9	i-C_4H_9	92	.....	99	2.0	1.4642	$C_{10}H_{20}ClNO$	17.24	17.43
H	s-C_4H_9	88	45–45.5	68	0.7	....	$C_6H_{12}ClNO$	23.69	24.06
s-C_4H_9	s-C_4H_9	80	.....	92	0.7	1.4681	$C_{10}H_{20}ClNO$	17.24	17.26
H	t-C_4H_9	75	82–83	..	..	....	$C_6H_{12}ClNO$	23.69	24.15
H	n-C_5H_{11}	89	.....	82	0.5	1.4665	$C_7H_{14}ClNO$	21.67	21.75
n-C_5H_{11}	n-C_5H_{11}	82	.....	126	1.0	1.4651	$C_{12}H_{24}ClNO$	15.17	15.25
i-C_5H_{11}	i-C_5H_{11}	89	.....	109	0.6	1.4625	$C_{12}H_{24}ClNO$	15.17	15.37
$CH_3(CH_2)_3CH(C_2H_5)CH_2$–	$CH_3(CH_2)_3CH(C_2H_5)CH_2$–	63	.....	154	0.8	1.4622	$C_{18}H_{38}ClNO$	11.18	11.32
H	n-$C_{14}H_{29}$–	77	64–65	..	..	....	$C_{16}H_{32}ClNO$	12.23	12.27
H	$CH_3CHClCH_2$–	85	.....	88	1.5	1.4942	$C_5H_9Cl_2NO$	41.70	41.62
H	$ClCH_2CH_2CH_2$–	86	36–37	..	..	....	$C_5H_9Cl_2NO$	41.70	41.87
H	$ClCH_2CHClCH_2$–	63	65–66	..	..	....	$C_5H_8Cl_3NO$	52.02	52.18
$CH_3CHClCH_2$–	$CH_3CHClCH_2$–	91	.....	134	0.7	1.5018	$C_8H_{14}Cl_2NO$	43.14	43.18
$ClCH_2CHClCH_2$–	$ClCH_2CHClCH_2$–	96[b]	.....	..	..	....	$C_8H_{12}Cl_6NO$	56.19	56.29[b]
H	$CH_3OCH_2CH_2CH_2$–	71	30	88	0.5	1.4712[a]	$C_6H_{12}ClNO_2$	21.41	21.45
H	$(CH_3)_2CHOCH_2CH_2CH_2$–	87	.....	92	0.5	1.4625	$C_6H_{14}ClNO_2$	18.31	18.27
CH_2=CH—CH_2–	CH_2=CH—CH_2–	91	.....	92	2.0	1.4932	$C_8H_{12}ClNO$	20.42	20.55
H	CH_2=$C(CH_3)CH_2$–	84	.....	96	1.0	1.4860	$C_4H_{10}ClNO$	24.02	24.03
CH_2=$C(CH_3)CH_2$–	CH_2=$C(CH_3)CH_2$–	70	.....	110	2.2[d]	1.4882	$C_{10}H_{18}ClNO$	17.58	17.77
H	CH_2=$CClCH_2$–	83	.....	101	1.4	1.5078	$C_5H_7Cl_2NO$	42.21	42.56
H	ClCH=CH—CH_2–[c]	69	52–53.5	112	0.5	....	$C_5H_7Cl_2NO$	42.21	42.22
H	$ClCH$=$CClCH_2$–	85	.....	126–131	1.8	1.5311	$C_5H_6Cl_2NO$	52.48	52.76
CH_2=CCl—CH_2	CH_2=CCl—CH_2–	86	.....	130	2.1[e]	1.5220	$C_8H_{10}Cl_3NO$	43.85	44.12
ClCH=CH—CH_2–[f]	ClCH=CH—CH_2–	80	.....	140–145	1.0	1.5220	$C_8H_{10}Cl_3NO$	43.85	43.97
CH≡C—CH_2–	CH≡C—CH_2–	67	.....	93	0.5	1.5120	C_8H_8ClNO	20.91	21.03
H	C_6H_{11}	94	108.5–109.5[g]	..	..	....	$C_8H_{14}ClNO$	20.19	20.42
CH_3	C_6H_{11}	84	.....	134	3.8	1.5005	$C_9H_{16}ClNO$	18.69	18.91
C_2H_5	C_6H_{11}	99	.....	120	1.1	1.4978	$C_{10}H_{18}ClNO$	17.40	17.64
CH_2=$CHCH_2$–	C_6H_{11}	81	.....	119	0.5	1.5079	$C_{11}H_{18}ClNO$	16.43	16.85
C_6H_{11}	C_6H_{11}	80	114.5–115.5	..	..	....	$C_{14}H_{24}ClNO$	13.76	13.85
H	C_5H_5O[i]	77	58–58.5	..	..	....	$C_7H_8ClNO_2$	20.42	20.62
H	C_4H_9O[k]	84	62.5–63.5	..	..	....	$C_7H_{12}ClNO_2$	19.96	20.12
H	C_5H_5S[l]	69	71.6–72.6	..	..	....	C_7H_8ClNOS	18.69	18.80
–$CH_2CH_2CH_2CH_2$–		51	44–46	112	0.5	....	$C_6H_{10}ClNO$	24.02	24.26
–$CH(CH_3)CH_2CH_2CH_2CH_2$–		88	.....	103	1.1	1.5012	$C_8H_{14}ClNO$	20.18	20.50
–$CH_2CH(CH_3)CH_2CH_2CH_2$–		82	.....	107	1.8	1.4976	$C_8H_{14}ClNO$	20.18	20.31
–$CH_2CH_2CH(CH_3)CH_2CH_2$–		76	.....	114	0.8	1.4966	$C_8H_{14}ClNO$	20.18	20.30
–$CH(CH_3)CH_2CH(CH_3)CH_2CH_2$		90	.....	118	1.0	1.4945	$C_9H_{14}ClNO$	18.69	18.82
–$CH(CH_3)CH_2CH_2CH_2CH(CH_3)$–		90	80–81.5	..	..	....	$C_9H_{16}ClNO$	18.69	19.20
–$CH(CH_3)CH_2CH(CH_3)CH_2CH(CH_3)$–		87	.....	123	2.0	1.4930	$C_{10}H_{18}ClNO$	17.40	17.78
–$CH(CH_3)CH_2CH_2CH(C_2H_5)CH_2$–		90	.....	124	0.7	1.4951	$C_{10}H_{18}ClNO$	17.40	17.78
CH_2=$CClCH_2$	C_6H_5	74	.....	138	0.7	1.5602	$C_{11}H_{11}Cl_2NO$	29.01	29.35
C_2H_5	4-ClC_6H_4	66	70–71	..	..	....	$C_{10}H_{11}Cl_2NO$	30.55	30.55
H[h]	2,4-$Cl_2C_6H_3$	84	101–102	..	..	....	$C_8H_6Cl_3NO$	44.62	44.46
H[h]	2,5-$Cl_2C_6H_3$	85	116–117	..	..	....	$C_8H_6Cl_3NO$	44.62	44.75
H	2-Cl-4-$NO_2C_6H_3$	91	118–119	..	..	....	$C_8H_6Cl_2O_3$	28.48	28.77
H	2,4-$(NO_2)_2C_6H_3$	96	114–114.5[j]	..	..	....	$C_8H_6ClN_3O_5$	13.65	13.72
$C_6H_5CH_2$–	$C_6H_5CH_2$–	74	.....	190	1.8	1.5837	$C_{16}H_{16}ClNO$	12.95	13.25
H	2,4-$Cl_2C_6H_3CH_2$–	82	96.5–97.5	..	..	....	$C_9H_8Cl_3NO$	42.12	42.23
H	3,4-$Cl_2C_6H_3CH_2$–	72	105–106	..	..	....	$C_9H_8Cl_3NO$	42.12	42.10

[a] On super cooled liquid. [b] On crude material. Decomposition occurred on attempted distillation under reduced pressure. [c] Prepared from *trans*-3-chloroallylamine hydrochloride. [d] F. Becke and G. Hummel, German Patent 812,376; *C. A.*, **46**, 11566 (1952), report b.p. 133–135° (20 mm.). [e] Ref. *d*, b.p. 161–163° (12 mm.). [f] Mixture of *cis–trans* isomers. [g] M. Backes, *Compt. rend.*, **233**, 66 (1951), reports m.p. 105–106°, 56% yield. [h] H. E. Thompson, *et al.*, *Botan. Gaz.*, **107**, 476 (1946), reported only on phytotoxicity. [i] N. G. Clark and A. F. Hams, *Biochem. J.*, **55**, 839 (1953), report m.p. 111–112°; 76% yield. [j] 2-Furfuryl. [k] 2-Tetrahydrofurfuryl. [l] 2-Thenyl.

2-Chloro-N-(2,3-dichloropropyl)-acetamide and N,N-bis-(2,3-dichloropropyl)-2-chloroacetamide were prepared by controlled chlorination of the respective allyl-2-chloroacetamides. Addition of chlorine to a carbon tetrachloride solution of the allyl compounds was accompanied by evolution of hydrogen chloride indicating chlorination in the α-position.

The intermediate chloropropylamine hydrochlorides were prepared from the corresponding alkanol

amines by conversion to the hydrochlorides and reaction with thionyl chloride in dry 1,2-dichloroethane.

The phthalimide method proved particularly useful for the preparation of chloroallyl- and benzylamines since the reaction of the halide and potassium phthalimide in dimethylformamide occurs under relatively mild conditions. The N-(substituted)-phthalimides were converted to the free amines by reaction with aqueous hydrazine hydrate.[3] This method gave higher yields than the hexamethylenetetramine procedure.

In the preparation of N-(3-chloroallyl)-phthalimide, the geometrical isomers were isolated by crystallization from ethanol. The infrared absorption spectra of the two isomers showed the lower melting isomer (m.p. 55.5–57°) to be *cis*. Treatment of crude *cis-trans*-N-(3-chloroallyl)-phthalimide with aqueous hydrazine hydrate gave rise to the isomeric amine hydrochlorides in impure form. The α-isomer melted at 209–210°, the β-isomer at 198–202° and a mixture of the two melted at 190°. After repeated crystallizations the melting points or the analyses did not change appreciably.

The correlation of structure of the amine hydrochlorides with the isomeric N-(3-chloroallyl)-phthalimides has not been made. This work, as well as the conversion of *cis*- and *trans*-3-chloroallylamine to the corresponding 2-chloroacetamides and the correlation of the isomers with *cis*- and *trans*-1,3-dichloropropene, is under investigation in this Laboratory. The configurations of the 1,3-dichloropropenes have been established and related to 3-substituted-1-chloropropenes.[4]

No attempt was made to isolate the isomeric N-(2,3-dichloroallyl)-phthalimides nor the *cis-trans* 2,3-dichloroallylamines.

Other amines used in the course of this work were either commercially available or synthesized as reported by other workers.

Experimental[5]

Preparation of 2-Chloroacetamides and Acetanilides. N-Butyl-2-chloroacetamide.—To a mixture of 29.3 g. of butylamine, 100 g. of 20% sodium hydroxide solution and 150 ml. of 1,2-dichloroethane, there was added 56.3 g. of chloroacetyl chloride at −10 to −15° during 45 minutes. The temperature was allowed to rise to 10° and the aqueous layer separated and washed with two 20-ml. portions of solvent. The dichloroethane solutions were combined, washed successively with 5% hydrochloric acid, 5% sodium bicarbonate solution and water, and dried over anhydrous magnesium sulfate. After removal of the solvent under reduced pressure, N-butyl-2-chloroacetamide was distilled through a 6" column packed with glass helices.

In the case of solids, the crude material was recrystallized from an appropriate solvent: petroleum ether, b.p. 60–70°, petroleum ether (b.p. 60–70°)–benzene mixture, benzene, aqueous ethanol or aqueous methanol.

2,2′-Dichloro-4-nitroacetanilide.—To a solution of 34.5 g. of 2-chloro-4-nitroaniline in 150 ml. of dry benzene there was added 34 g. of chloroacetyl chloride during 15–30 minutes. The solution was heated at reflux (4–8 hours) until hydrogen chloride was no longer evolved. Upon cooling, the α-chloroacetanilide crystallized. It was collected on a filter, washed with cold solvent and recrystallized from benzene.

In other preparations, it was necessary to remove the benzene by distillation and to crystallize the acetanilide by addition of petroleum ether, b.p. 60–70°. A mixture of petroleum ether, b.p. 60–70° and benzene proved quite satisfactory for recrystallizations.

2-Chloro-N-(2,3-dichloropropyl)-acetamide.—To 290 ml. of carbon tetrachloride saturated with chlorine (23 g., 0.32 mole), there was added 36 g. (0.27 mole) of N-allyl-2-chloroacetamide in 100 ml. of carbon tetrachloride at 0–5° during 2.5 hours. Stirring was continued for 1/2 hour. An assay of the solution indicated that 0.27 mole of chlorine had been consumed. The solvent was removed under reduced pressure and the residue dissolved in 1,2-dichloroethane. The solution was washed with water and dilute sodium bicarbonate, and dried over magnesium sulfate. Removal of the solvent left an oil (n^{25}D 1.5165) which solidified on standing; yield 42.8 g. (87%). Recrystallization from aqueous ethanol afforded material melting at 65–66°.

N,N-Bis-(2,3-dichloropropyl)-2-chloroacetamide was prepared similarly in 96% crude yield. This material could not be induced to crystallize and decomposed on distillation at 2 mm.

Preparation of Intermediates. Di-(2-chloropropylamine) Hydrochloride.—The procedure is a modification of that given for 2-chloroethylamine hydrochloride by Ulrich.[6] Diisopropanolamine hydrochloride was prepared by the addition of 119 g. of concentrated hydrochloric acid to 113 g. of diisopropanolamine at 40–50°. The solution was concentrated to a small volume by distillation under reduced pressure. 1,2-Dichloroethane (680 ml.) was added and the last traces of water removed by azeotropic distillation. To an anhydrous suspension of amine hydrochloride there was added 262 g. of thionyl chloride at 55–60° during 4 hours. The mixture was held at 60–65° for 2 hours and then about 100 ml. of solvent, together with excess thionyl chloride, was removed at 100–150 mm. The suspension of chloroamine hydrochloride was cooled, filtered and the product washed with fresh solvent. The yield was 161 g. (78%); m.p. 196–199°. The melting point did not change on recrystallization from ether–ethanol mixture.

Anal. Calcd. for $C_6H_{13}Cl_2N\cdot HCl$: total Cl, 51.50; ionic Cl, 17.17. Found: total Cl, 51.76; ionic Cl, 17.17.

3-Chloropropylamine Hydrochloride.—This compound was prepared in the above manner from 3-aminopropanol. The yield of crude material was 91%; m.p. 136–139°. Recrystallization from ether–ethanol mixture raised the melting point to 142.8–144.6°.

Anal. Calcd. for $C_3H_8ClN\cdot HCl$: total Cl, 54.54; ionic Cl, 27.27. Found: total Cl, 54.59; ionic Cl, 27.48.

Other chloroalkyl amine hydrochlorides which were used in the preparation of the α-chloroacetamides listed in Table I were prepared as described above. The physical constants agreed with those given in the literature.

2-Chloroallylamine Hydrochloride.—A solution of 70 g. of hexamethylenetetramine and 55 g. of 2,3-dichloropropene in 500 ml. of chloroform was refluxed (64°) for 16 hours during which time the hexamine salt precipitated. After cooling to room temperature, the solid was collected on a filter, washed with chloroform and dried; yield 62 g. (50%); m.p. 176–178°.

Anal. Calcd. for $C_9H_{16}Cl_2N_4$: ionic Cl, 14.12. Found: ionic Cl, 14.37.

A mixture of 190 g. of the hexamethylenetetramine salt of 2,3-dichloropropene, 690 ml. of ethanol and 340 ml. of concentrated hydrochloric acid was stirred at room temperature overnight. The precipitated ammonium chloride was filtered and washed with ethanol, and the combined filtrates were concentrated by distillation. Acetone was added to the residue and the solid consisting of a mixture of amine hydrochloride and ammonium chloride was filtered. A second crop was recovered from the mother liquors by removal of the acetone and azeotropic distillation of the residual water with benzene. The two crops were treated separately by solution in absolute ethanol to remove ammonium chloride and reprecipitated by addition of ether; combined yield 57.5 g. (59%). A portion was recrystallized twice from ethanol–ether mixture for analysis; m.p. 212–213°.

Anal. Calcd. for $C_3H_6ClN\cdot HCl$: total Cl, 55.40; ionic Cl, 27.70. Found: total Cl, 55.50; ionic Cl, 27.75.

(3) H. R. Ing and R. H. F. Manske, *J. Chem. Soc.*, 2348 (1926).

(4) W. C. Wolfe, H. M. Doukas and J. S. Ard, THIS JOURNAL, **76**, 627 (1954).

(5) Melting points are uncorrected. We are indebted to Mr. A. Bybell for analyses and to Mr. O. Kinast for infrared absorption spectra.

(6) H. Ulrich and E. Ploetz, U. S. Patent 2,163,181.

N-(3-Chloroallyl)-phthalimide.—To 500 ml. of dimethylformamide, there was added 136 g. of potassium phthalimide and 82 g. of 1,3-dichloropropene. The mixture was stirred at 60–95° for 4 hours, cooled and poured into 1.5 liters of water. The solid was filtered and washed with water; yield 150 g. (95%); m.p. 89–93°. The crude consisted of a mixture of the *cis* and *trans* isomers. Five grams of the crude recrystallized from 45 ml. of ethanol and 110 ml. water gave material (α) melting at 109–111°. Addition of water to the mother liquors gave the other isomer (β); m.p. 62–65°. The higher melting isomer (α), recrystallized from ethanol, melted at 112–113°. The β-isomer recrystallized twice from 50% ethanol melted at 55.5–57°. Infrared analysis indicated the α-isomer to be *trans* and the β-isomer to be *cis*.

Anal. Calcd. for $C_{11}H_8ClNO_2$: Cl, 15.99; N, 6.32. Found: α-isomer, Cl, 15.92; N, 6.36; β-isomer, Cl, 16.29; N, 6.13.

N-(2,3-Dichloroallyl)-phthalimide prepared from *cis-trans*-1,2,3-trichloropropene as described above, melted at 89–98°; 96% yield. A sample recrystallized from dilute ethanol melted at 102–109°. No attempt was made to isolate the *cis* and *trans* isomers which undoubtedly are responsible for the range in melting point.

Anal. Calcd. for $C_{11}H_7Cl_2NO_2$: Cl, 27.69. Found: Cl, 27.30.

N-(2,4-Dichlorobenzyl)-phthalimide prepared according to the above method in quantitative yield melted at 180–182°. A sample for analysis was recrystallized from ethanol; m.p. 182–183°.

Anal. Calcd. for $C_{15}H_9Cl_2NO_2$: Cl, 23.16. Found: Cl, 22.62.

N-(3,4-Dichlorobenzyl)-phthalimide similarly prepared in quantitative yield melted at 152–154°. A portion recrystallized from ethanol melted at 155–156°.

Anal. Calcd. for $C_{15}H_9Cl_2NO_2$: Cl, 23.16. Found: Cl, 22.85.

N-3-Chloroallylamine Hydrochloride.—A suspension of 129 g. of N-(3-chloroallyl)-phthalimide (crude *cis–trans* mixture) in 450 ml. of methanol and 41.0 g. of 85% aqueous hydrazine hydrate was heated to reflux (68°) in ½ hour. The clear solution suddenly became almost completely solid. It was held at 68° for 2 hours, and cooled to room temperature. After the addition of 100 ml. of water and 150 ml. of concentrated hydrochloric acid, the thick slurry was heated at reflux for 2 hours. The phthalyl hydrazide (89 g., 94%) was filtered at room temperature and washed with ethanol and water. The combined filtrates were reduced to a small volume and upon addition of acetone, the amine hydrochloride precipitated. It was collected on a filter and washed with dry acetone; α-isomer, yield 38.5 g. (52%); m.p. 180–197°. Concentration of the acetone mother liquors and removal of last traces of water by azeotropic distillation with benzene gave 49 g. of crude material which was contaminated with hydrazine hydrochloride. This was removed by digesting with absolute ethanol and filtering. Addition of ether to the alcohol solution gave the β-isomer; 35 g. (47.5%); m.p. 137–170°. Total yield of both crops amounted to 73.5 g. (99%).

Two recrystallizations of the α-isomer from ethanol gave material melting at 209–210°. The β-isomer on recrystallization from absolute ethanol melted at 198–202°. A mixture of the two isomers melted at 190°. The melting points were not changed on further recrystallization.

Anal. Calcd. for $C_3H_6ClN\cdot HCl$: total Cl, 55.40; ionic Cl, 27.70. Found: α-isomer, total Cl, 54.79; ionic Cl, 27.56; β-isomer, total Cl, 55.37; ionic Cl, 28.50.

2,3-Dichloroallylamine was prepared as described above from the corresponding phthalimido derivative. The combined filtrates (after removal of phthalyl hydrazide) were reduced to about one-half the original volume under reduced pressure, made strongly alkaline with 50% sodium hydroxide solution and extracted with ether. After drying over magnesium sulfate, the solvent was removed to give the crude amine in 86% yield; $n^{25}D$ 1.4956.

The **hydrochloride** melted at 153–168° after recrystallization from ether–ethanol mixture. No attempt was made to isolate the geometrical isomers which are undoubtedly responsible for the wide range in melting point.

Anal. Calcd. for $C_3H_5Cl_2N\cdot HCl$: total Cl, 65.49; ionic Cl, 21.83. Found: total Cl, 65.40; ionic Cl, 21.90.

2,4-Dichlorobenzylamine was prepared from the phthalimido derivative as described for 2,3-dichloroallylamine in 73% crude yield; $n^{25}D$ 1.5760.

The **hydrochloride**, prepared from concentrated hydrochloric acid in ethanol, melted at 270–272°.

Anal. Calcd. for $C_7H_7Cl_2N\cdot HCl$: total Cl, 50.05; ionic Cl, 16.68. Found: total Cl, 49.98; ionic Cl, 16.66.

3,4-Dichlorobenzylamine was prepared in an analogous manner from the phthalimido derivative in 91% crude yield; $n^{25}D$ 1.5658.

The **hydrochloride**, prepared by the addition of concentrated hydrochloric acid to the crude amine in ethanol, melted at 237–239° after recrystallization from ethanol.

Anal. Calcd. for $C_7H_7Cl_2N\cdot HCl$: total Cl, 50.05; ionic Cl, 16.68. Found: total Cl, 49.78; ionic Cl, 16.60.

Di-3-chloroallylamine.[7]—This compound was prepared by the cyanamide method as given for diallylamine[8] in 75% yield; b.p. 100–106° (15–18 mm.).

The intermediate, **di-(3-chloroallyl)-cyanamide**, boiled at 129–162°, $n^{25}D$ 1.5142; 43.5% yield. The wide range in b.p. may be due to the *cis–trans* mixture.

Anal. Calcd. for $C_7H_8Cl_2N_2$: Cl, 37.06. Found: Cl, 36.74.

Di-2-chloroallylamine.[9]—This was also prepared as described above but the cyanamide was used directly without purification. The amine distilled at 69° (9 mm.).

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