diethyl- and di-*n*-butylamines may have been due to partial reaction between the secondary amines and the benzaldehyde, and not to presence of primary amine impurities.

Application to Mixtures Containing Ammonia.—Application of the method to known mixtures of di-*n*-butylamine, *n*-butylamine, and ammonia indicated that the secondary amine could be determined accurately in the presence of up to at least 7% ammonia by weight. In the presence of much water, however, high results were obtained when large amounts of ammonia were also present, as illustrated in Fig. 1.

The validity of the procedure to be applied to samples containing both ammonia and water was tested as follows: Known mixtures containing ammonia, a primary amine, or a primary amine plus a secondary amine, were neutralized with hydrochloric acid and the ammonium ions were removed and determined by precipitation with the cobaltinitrite reagent. The filtrate in each case was made basic with sodium hydroxide and the liberated amines were distilled into methanol and determined by acidimetric titration in the cases of single amines or by acidimetric titration plus the azomethine procedure when both primary and secondary amines were present. Typical results on several of such mixtures are tabulated in Table II. The ammonia separation is not applicable in the presence of methylamine, since the methylammonium cobaltinitrite precipitate is apparently not very soluble.

TABLE II

ANALYSES OF MIXTURES CONTAINING AMMONIA BY PRECIPITATION OF AMMONIA AND DETERMINATION OF AMINES RECOVERED AFTER THE AMMONIA SEPARATION

Amines in sample	Ammonia, grams		Primary amine, grams		Secondary amine, grams	
	Present	Found	Present	Found	Present	Found
n-Butyl	0.0148	0.014	7.22	7.10		
Allyl	.0205	.0199	1.89	1.84		
Ethyl	.0205	.0208	1.175	1.155		
Cyclohexyl	.0204	.0202	2.56	2.49		
Isopropyl and	.0138	.0135	0.0979	0.0947	3.24	3.20
diisopropyl	.0691	.0675	.326	.323	0.810	0.799
Di-*n*-butyl and *n*-butyl	.1232	.1199	.822	.776[a]	2.015	1.922[a]

[a] Recovery of higher-boiling amines is not complete by the prescribed distillation procedure.

Acknowledgment.—The authors wish to thank Dr. L. Lykken for his helpful advice, especially in connection with the electrometric aspects of this work.

Summary

1. A new acidimetric method of general applicability has been developed for the determination of secondary aliphatic amines in the presence of primary amines and ammonia. The method depends upon the fact that salicylaldehyde reacts quantitatively with primary amines and ammonia to form compounds of decreased basicity.

2. With this method tertiary amines analyze as secondary amines, since neither type reacts with salicylaldehyde. Ammonia in the absence of water reacts like a primary amine and does not interfere with the secondary amine determination. Water in the absence of ammonia has no effect on the analysis.

3. Ammonia in a mixture with aliphatic amines may be determined by precipitation with sodium cobaltinitrite followed by distillation of ammonia from the precipitate decomposed with alkali. Tertiary amines in such mixtures may be readily determined by acetylating the mixture and titrating the mixture with perchloric acid in acetic acid. Therefore, with the aid of a total base determination, all four components of a mixture containing tertiary amine, secondary amine, primary amine, and ammonia may be quickly and accurately determined using acidimetric procedures.

EMERYVILLE, CALIFORNIA RECEIVED MARCH 10, 1947

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

Allylic Chlorides. III. Preparation of the 1,3-Dichloro-2-methyl-1-propenes

BY LEWIS F. HATCH, JOHN J. RUSS[1] AND LEON B. GORDON

In the course of current studies on the influence of geometrical configuration on chemical reactivity[2,3] it became desirable to prepare both pure *cis* and pure *trans* 1,3-dichloro-2-methyl-1-propene. The synthesis of these dichlorides has been attempted by the chlorination of both isobutylene and methallyl chloride,[4] dehydration of 1,3-dichloro-2-methyl-2-propanol,[4b] pyrolysis of 1,2,3-trichloro-2-methylpropane[5] and by the dehydrochlorination of 1,2,3-trichloro-2-methylpropane by the action of quinoline.[6] In every case either only one isomer was formed or the mixture of isomers produced was not resolved. It has, however, been suggested by Mooradian and Cloke[7] that this might be accomplished through the hydroxyl derivatives.

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[1] Present address: Magnolia Petroleum Co., Dallas, Texas.

[2] Hatch and Roberts, THIS JOURNAL, **68**, 1196 (1946).

[3] Hatch, Gordon and Russ, paper presented at the Texas Regional Meeting of the American Chemical Society, Dallas, Texas, December 13, 1946.

[4] (a) Burgin, Engs, Groll and Hearne, *Ind. Eng. Chem.*, **31**, 1413 (1939); (b) D'yakonov, *J. Gen. Chem. U. S. S. R.*, **10**, 402 (1940); (c) Burgin, Hearne and Rust, *Ind. Eng. Chem.*, **33**, 385 (1941); (d) Suter and Bordwell, THIS JOURNAL, **65**, 507 (1943); (e) Pogorshelski, *J. Russ. Phys.-Chem. Soc.*, **36**, 1129 (1904).

[5] Rogers and Nelson, THIS JOURNAL, **58**, 1029 (1936).

[6] Mooradian and Cloke, *ibid.*, **68**, 785 (1946).

[7] Mooradian and Cloke, *ibid.*, **67**, 942 (1945).

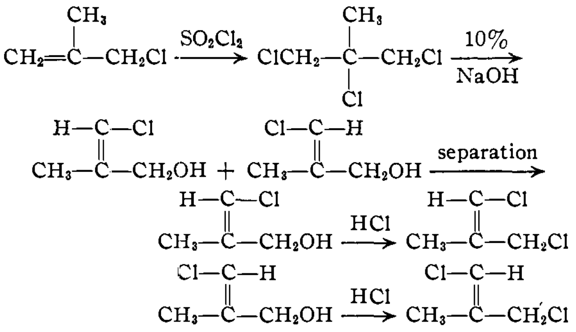
TABLE I

1,3-DICHLORO-2-METHYL-1-PROPENE AND RELATED COMPOUNDS

		1,3-Dichloro-2-methyl-1-propene (low boiling)	1,3-Dichloro-2-methyl-1-propene (high boiling)	3-Chloro-2-methyl-2-propen-1-ol (low boiling)	3-Chloro-2-methyl-2-propen-1-ol (high boiling)	1,2,3-Trichloro-2-methylpropane	3-Chloro-2-chloromethyl-1-propene
Boiling point, °C. (mm.)		130(741)	132.0(745)	160.5(742)	167.4(743)	108.5(150)	85(150)
						160–164[a]	138–138.3[b]
Index of refraction	n^{20}D				1.4702	1.4745[g]	1.4751[e]
				1.4737[d]	1.4730[d]	1.4765[d]	1.4754[b]
(Abbé)	n^{25}D	1.4698	1.4740	1.4703	1.4691	1.4724[g]	1.4728
	n^{30}D	1.4675	1.4712	1.4675			1.4705
Density	d^{20}_4			1.1292	1.1251		1.1778[e]
				1.1292[c]			1.1782[b]
	d^{25}_4	1.1629	1.1667	1.1248	1.1206	1.3002[g]	1.1722
				1.1290[d,f]	1.1262[d,f]	1.3020[d]	
	d^{30}_4	1.1571	1.1612	1.1200			1.1666
Molecular refrac.	Calcd.	29.94	29.94	26.60	26.60		29.94
	Found	29.97	30.08	26.43	26.46		29.92
Anal., % Cl	Calcd.	56.73	56.73	33.28	33.28	65.9	
	Found	56.85 56.88	56.82 56.85	33.08 33.28	33.16 33.30	65.5 65.9	

[a] Mooradian and Cloke, THIS JOURNAL, **68,** 785 (1946). [b] Mooradian and Cloke, *ibid.*, **67,** 942 (1945). [c] Pogorshelski, *J. Russ. Phys.-Chem. Soc.*, **36,** 1129 (1904); *Chem. Zentr.*, **76,** 688 (1905). [d] Rogers and Nelson, THIS JOURNAL, **58,** 1029 (1936). [e] Extrapolated value. [f] This figure is in good agreement with those reported at 20°. It is suggested that inasmuch as Rogers and Nelson reported the index of refraction measurements at 20° they may also have determined the densities at 20°. [g] These figures have been checked on the trichloride prepared by several different methods.

The present paper describes the preparation of both the *cis* and *trans* isomers of 1,3-dichloro-2-methyl-1-propene from the corresponding β-chloro-methallyl alcohols (3-chloro-2-methyl-2-propen-1-ol). A mixture of the β-chloro-alcohols was obtained by refluxing 1,2,3-trichloro-2-methylpropane with 10% sodium hydroxide.[5] The two isomers were then separated by a Podbielniak Hyper-Cal distillation column. The trichloride was obtained by the action of sulfuryl chloride on methallyl chloride.[6]



Various physical data for both of the dichlorides as well as several intermediate compounds are given in Table I. Data for the two 1,3-dichloro-2-methyl-1-propenes have not been reported previously. Data in the prior literature have been for only the lower boiling isomer or for mixtures of the two isomers which probably contained a high percentage of the lower boiling isomer.

At the start of this investigation it was thought that a simple method of preparing the 1,3-dichloro-2-methyl-1-propenes would be by the chlorination of methallyl chloride. The mixture of the two dichlorides would be hydrolyzed, the β-chloro-alcohols separated and reconverted to the corresponding dichlorides. This method was unsuccessful because the hydrolysis of the mixture of 1,3-dichloro-2-methyl-1-propenes apparently yields only the low boiling chloro-alcohol. A study of Pogorshelski's[4c] data leads to the same conclusion.

Experimental

Chlorination of Methallyl Chloride.—Chlorine was passed into a mixture of 3 moles of methallyl chloride[8] and 300 ml. of carbon tetrachloride at 20–30° until free chlorine was detected in the effluent hydrogen chloride. The reaction mixture was washed free of hydrogen chloride, dried and then distilled at 150 mm. pressure through a 3-foot glass helix-packed column. The following yields were obtained: 1,3-dichloro-2-methyl-1-propene (b. p. 81° (150 mm.), n^{25}D 1.4710) 33%; 3-chloro-2-chloromethyl-1-propene (b. p. 85° (150 mm.), n^{25}D 1.4728) 25% and 1,2,3-trichloro-2-methylpropane (b. p. 108.5° (150 mm.), d^{25}4 1.3002) 26%; bottoms (as tetrachloride) 10%.

Two moles of the 1,3-dichloro-2-methyl-1-propene fraction (80–83°, 150 mm.) were hydrolyzed with a 10% excess of 10% sodium carbonate and extracted several times with diethyl ether. The extract was dried over magnesium sulfate and, after removal of the ether, distilled at 25 mm. pressure. A center portion of the 3-chloro-2-methyl-2-propen-1-ol fraction gave the following constants: b. p. 76° (25 mm.); d^{25}_4 1.1247. The 3,5-dinitrobenzoate had a melting point of 93.5°. Rogers and Nelson report 94.4–95.8° for the low boiling isomer and 63.8° for the high boiling isomer.

By comparing these physical constants with the constants given in Table I, which are the best available, it appears as if the hydrolysis of the 1,3-dichloro-2-methyl-1-propenes gives substantially only the low boiling isomer of 1-chloro-2-methyl-2-propen-1-ol.

1,2,3-Trichloro-2-methylpropane.—The 1,2,3-trichloro-2-methylpropane was prepared by the chlorination of 1,2-dichloro-2-methylpropane and by the chlorination of methallyl chloride using sulfuryl chloride. The 1,2-

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(8) Commercial grade methallyl chloride was furnished us for this work by the Shell Development Co., Emeryville, California.

dichloro-2-methylpropane was prepared in a 77% yield by treating methallyl chloride with concentrated hydrochloric acid for twenty-four hours at 60–65°. The dichloride had the following constants; b. p. 107° (745 mm.); $n^{25}\mathrm{D}$ 1.4362; lit. b. p. 108°; $n^{25}\mathrm{D}$ 1.4368.

Four and one-half moles of 1,2-dichloro-2-methylpropane was chlorinated at 60° by passing in chlorine at the rate of 333 cc. per minute. The dichloride was vigorously stirred and illuminated by a 250-watt light placed 3 inches from the flask. The chlorination was discontinued when sufficient time had elapsed for approximately 50% chlorination. The reaction mixture was washed free of hydrogen chloride, dried and distilled, yield of 1,2,3-trichloro-2-methylpropane (106.5–109.0° at 150 mm.) was 56%.

Because the direct chlorination of neither methallyl chloride nor 1,2-dichloro-2-methylpropane gave good yields of 1,2,3-trichloro-2-methylpropane, the method of Mooradian and Cloke[6] for the chlorination of methallyl chloride with sulfuryl chloride was used to prepare most of the trichloride used in this investigation. Yields comparable to theirs were obtained.

3-Chloro-2-methyl-2-propen-1-ol.—The 3-chloro-2-methyl-2-propen-1-ol was prepared by the dehydrochlorination and hydrolysis of 1,2,3-trichloro-2-methylpropane with 10% sodium hydroxide. The reaction vessel was a 5-liter, three-necked, round-bottomed flask fitted with a mercury sealed stirrer, West reflux condenser and thermometer. The flask containing a 10% aqueous solution of sodium hydroxide was immersed in an oil-bath and the contents heated to boiling. The trichloride was then quickly added and the reaction mixture refluxed with vigorous stirring for three hours. The products of the reaction were distilled directly from the reaction mixture as an azeotrope with water. The azeotrope was saturated with sodium chloride, the organic layer separated and the water layer extracted three times with ether. The ether was removed from the ether extract on a steam cone and the residue added to the organic layer. This material was dried with magnesium sulfate and distilled through the 3-foot glass helix-packed column. Yields were 3-chloro-2-methyl-2-propen-1-ol, 65%; bottoms (as the ether of chloro-methallyl alcohol), 30%.

Separation of Low and High Boiling 3-Chloro-2-methyl-2-propen-1-ol.—The two isomers of 3-chloro-2-methyl-2-propen-1-ol were separated at 150 mm. pressure using a 13 mm. × 36″ Podbielniak Hyper-Cal distillation column with a reflux ratio of 75 to 1 and a take off rate of 5 ml. per hour. The course of the distillation was followed by both index of refraction and density. A portion with constant index of refraction and density was taken for each isomer to obtain the data given in Table I. The separation is not as easy as the differences in boiling points would indicate.

1,3-Dichloro-2-methyl-1-propene.—The 1,3-dichloro-2-methyl-1-propenes were prepared from the corresponding chloro-alcohols by treating the alcohols with concentrated hydrochloric acid (mole ratio: 1 to 4) on a steam cone for fifteen minutes and then permitting the mixture to stand for twelve hours at room temperature. The organic layer was separated, washed free of acid and dried over magnesium sulfate. The chlorides were distilled at 150 mm. pressure and a center fraction taken for the determination of the constants given in Table I; yields were 72%.

Subsequent hydrolysis of each isomeric dichloride regenerated the original isomeric chloro-alcohol.

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Summary

The two geometrical isomers of 1,3-dichloro-2-methyl-1-propene have been prepared and index of refraction, density and boiling point of each isomer have been obtained.

More accurate indexes of refraction, densities and boiling points have been obtained for 1,2,3-trichloro-2-methylpropane and the two geometrical isomers of 3-chloro-2-methyl-2-propen-1-ol.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Derivatives of Urethan; Azamalonic Esters[1]

BY L. G. R. TOMPKINS[1a] WITH ED. F. DEGERING

Azamalonic esters are compounds analogous to the malonic esters but having a nitrogen atom in place of the methylene carbon atom. A series of these esters has been prepared by us and will be studied for possible pharmacological activity.

The unsubstituted azamalonic esters have been known as carbalkoxy urethans, imidodicarboxylic esters and carbalkoxy alkyl carbamates. The term "azamalonic ester" is used in this paper for its simplicity and unmistakable identity.

Considerable investigation of various types of urethans as physiological agents has been undertaken.[1b,2] Urethan, or ethyl carbamate, is a mild hypnotic and a feeble diuretic. It has proved disappointing from the clinical standpoint since it is rather weak in its action and an immunity is readily acquired. Other esters of carbamic acid, such as Aponal (tertiary amyl carbamate), Hedonal (secondary amyl carbamate), Aleudrin (dichloroisopropyl carbamate), and Voluntal (trichloroethyl carbamate), have been accepted for general clinical usage as hypnotics and sedatives. Generally the toxicity and depressant qualities of these compounds are greater than those of urethan itself.

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[1] Abstract of a thesis presented to the faculty of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, February, 1947. This work was sponsored by The Chattanooga Medicine Co. and the Purdue Research Foundation. Presented before the Division of Medicinal Chemistry, Atlantic City, April, 1947.

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