

m.p. 175° (source, styrene oxide dimerization); recrystallized from ether, acetone, and a mixture of these solvents; 2-benzyl-4-phenyl-1,3-dioxolane, m.p. 41–42°, recrystallized from ethanol and an ether-petroleum ether mixture; phenylethylene glycol, m.p. 66–67°, recrystallized from ether-petroleum ether.

Substances Available from Previous Work at These Laboratories.¹⁰—All compounds listed were recrystallized from an ether-petroleum ether mixture unless otherwise

(10) Summerbell and Bauer, *THIS JOURNAL*, **57**, 2364 (1935).

specified: monophenyl-1,4-dioxane, m.p. 46°, recrystallized from alcohol; 2,3-diphenyl-1,4-dioxane, m.p. 49–50°, recrystallized from petroleum ether; 2,3-dibenzyl-1,4-dioxane, m.p. 62°; 2,3-di-(*o*-tolyl)-1,4-dioxane, m.p. 105–106°; 2,3-di-(*m*-tolyl)-1,4-dioxane, m.p. 84°; 2,3-di-(4-chlorophenyl)-1,4-dioxane, m.p. 152–153°; 2,3-dixenyl-1,4-dioxane, m.p. 145–147°; mono-*p*-anisyl-1,4-dioxane, m.p. 64–66°; 2,3-di-(4-methoxyphenyl)-1,4-dioxane, m.p. 79–80°.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE DEFENSE RESEARCH LABORATORY, THE UNIVERSITY OF TEXAS]

Allylic Chlorides. XIX.¹ The Hydrochlorination Products of 2,3-Dimethyl-1,3-butadiene²

BY LEWIS F. HATCH AND GLEN E. JOURNEY

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The addition of hydrogen chloride to 2,3-dimethyl-1,3-butadiene yields a mixture of 1-chloro-2,3-dimethyl-2-butene and 3-chloro-2,3-dimethyl-1-butene while hydrochlorination in aqueous medium gives 1,3-dichloro-2,3-dimethylbutane in addition to these monochlorides. These findings are not in agreement with previous literature which characterizes 3-chloro-2,3-dimethyl-1-butene as 1-chloro-2,3-dimethyl-2-butene and lists it as the only product. A study has been made of the reactions of 1-chloro-2,3-dimethyl-2-butene with potassium iodide in acetone and sodium ethoxide in ethanol.

In the course of a study on allylic chlorides it became desirable to prepare 1-chloro-2,3-dimethyl-2-butene and a survey of the literature indicated that several methods for its preparation were available. Tishchenko³ reported the preparation of this compound by the chlorination of 2,3-dimethyl-2-butene in a manner similar to that used

butene. In 1947 Howard, *et al.*,⁵ reported the addition of hydrogen chloride to 2,3-dimethyl-1,3-butadiene in the presence of zinc chloride to obtain a quantitative yield of 1-chloro-2,3-dimethyl-2-butene. Because of the indicated high yield of the desired compound, the hydrochlorination of 2,3-dimethyl-1,3-butadiene was investigated. The results obtained, however, were not the same as those of Howard and co-workers.

It was found that the two synionic isomers, 1-chloro-2,3-dimethyl-2-butene and 3-chloro-2,3-dimethyl-1-butene, were produced by this method of hydrochlorinating 2,3-dimethyl-1,3-butadiene (Fig. 1) and that the relative amounts of the two isomers were dependent upon the temperature at which the reaction took place. Lower reaction temperatures favored the formation of the primary chloride, but the highest yield of this isomer was only 15% at –69°. The monochlorides did not undergo allylic rearrangement under the conditions of the hydrochlorination and no dichloride was produced.

The two monochlorides were characterized by their physical properties and by their infrared spectra. The lower boiling isomer, which is assumed to be the tertiary chloride, has an infrared spectrum containing an absorption at 11.2 μ caused by the RR'C=CH₂ structure. This band is absent in the higher boiling isomer. The 6.1 μ C=C stretching vibration, present in the spectrum of the lower boiling isomer, could not be detected in the spectrum of the higher boiling compound. It should be very weak in the nearly symmetrical primary chloride and is probably masked by the

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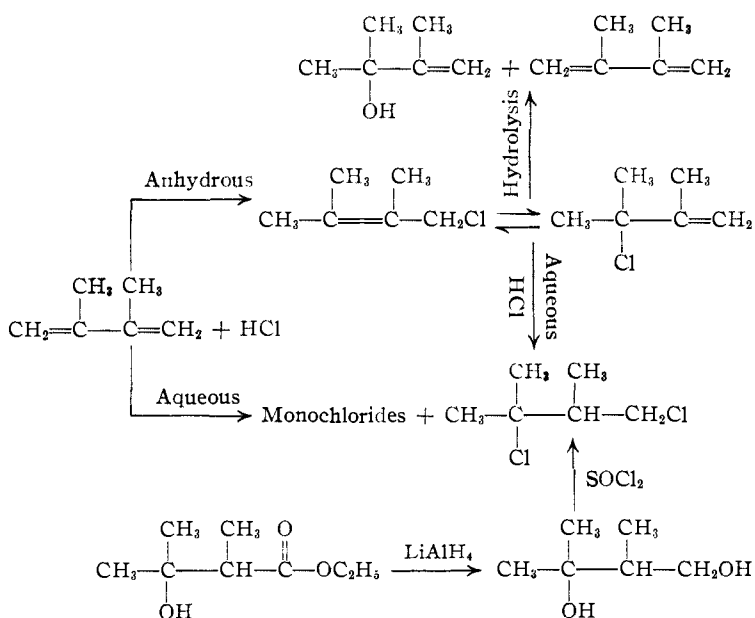


Fig. 1.—Hydrochlorination of 2,3-dimethyl-1,3-butadiene.

earlier by Chupotsky and Mariutza⁴ to prepare an uncharacterized monochloride which was later assumed to have been 1-chloro-2,3-dimethyl-2-

(1) For paper number XVIII of this series, see L. F. Hatch and D. W. McDonald, *THIS JOURNAL*, **74**, 3328 (1952).

(2) Presented in part at the 121st National Meeting of the American Chemical Society, Buffalo, New York, March, 1951.

(3) D. V. Tishchenko, *J. Gen. Chem. (U.S.S.R.)*, **8**, 1232 (1938); *C. A.*, **33**, 4130 (1939).

(4) A. Chupotsky and N. Mariutza, *J. Russ. Phys. Chem. Soc.*, **21**, 432 (1889); *Ber.*, **22**, 760 (1889).

(5) F. L. Howard, T. W. Mears, A. Fookson, P. Pomerantz and D. B. Brooks, *J. Research Natl. Bur. Standards*, **58**, 374 (1947).

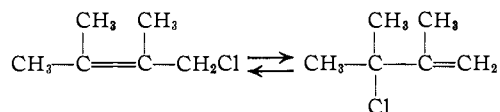
TABLE I
 PHYSICAL PROPERTIES

Compound	Temperature, °C. (mm.)	Index of refraction n_D^j	Density d_4^t
3-Chloro-2,3-dimethyl-1-butene	32(45) 113-114(752)	1.4380(20)	0.9053(20)
		1.4352(25)	.9004(25)
		1.4325(30)	.8955(30)
1-Chloro-2,3-dimethyl-2-butene	57.7(45) 32(45) ^a 111-112(756) ^b	1.4605(20)	.9355(20)
		1.4582(25)	.9311(25)
		1.4559(30)	.9268(30)
1,3-Dichloro-2,3-dimethylbutane	80-82(45) 161-163(760)	1.4315(19/C) ^b	.8895(19) ^b
		1.4559(20)	1.070(20)
		1.4538(25)	1.064(25)
2,3-Dimethyl-1,3-butanediol	95(12)	1.4517(30)	1.059(30)
		1.4462(20)	0.9680(20)
		1.4445(25)	.9645(25)
		1.4428(30)	.9610(30)

^a F. L. Howard, T. W. Mears, A. Fookson, P. Pomerantz and D. B. Brooks, *J. Research Natl. Bur. Standards*, **38**, 374 (1947). ^b D. V. Tishchenko, *J. Gen. Chem. (U.S.S.R.)*, **8**, 1232 (1938); *C. A.*, **33**, 4190 (1939).

water vapor spectrum. The higher boiling isomer has an absorption at 7.93μ which checks closely with the 7.94μ absorption of compounds of the type $RR'C=CR''CH_2Cl$. The very rapid reaction of the higher boiling isomer with potassium iodide and sodium ethoxide is also characteristic of a primary allylic chloride.

The various results in the literature and those obtained in the present study are accounted for by a relatively rapid allylic rearrangement between the two chlorides. Analysis of the equilibrium mixture both by index of refraction and infrared spectra



indicated the presence of about 87% 1-chloro-2,3-dimethyl-2-butene. The rearrangement is catalyzed by proton donors and inhibited by proton acceptors. Slow distillation of a mixture of the two isomers at atmospheric pressure gives only the lower boiling 3-chloro-2,3-dimethyl-1-butene. The two isomers can be separated by low temperature distillation and they can be stored without rearrangement at Dry Ice temperature. At room temperature they undergo allylic rearrangement fairly rapidly unless a proton acceptor is present.

The hydrochlorination of 2,3-dimethyl-1,3-butadiene by shaking it with concentrated hydrochloric acid in the presence of copper(I) chloride⁶ gave both monochlorides and in addition a small amount of 2,3-dichloro-2,3-dimethylbutane⁷ and an appreciable amount of 1,3-dichloro-2,3-dimethylbutane. The same dichlorides were also obtained by the hydrochlorination of a mixture of the two monochlorides under the same conditions. The structure of the 1,3-dichloro-2,3-dimethylbutane was established by synthesis from 2,3-dimethyl-1,3-butanediol which in turn was obtained by the lithium aluminum hydride reduction of the ethyl ester of 3-hydroxy-2,3-dimethylbutanoic acid (Fig. 1). The physical properties and infrared spectra of the two chlorides were the same in all essential respects. This dichloride is apparently

(6) W. H. Carothers, G. J. Berchet and A. M. Collins, *THIS JOURNAL*, **54**, 4066 (1932).

(7) C. Friedel and R. D. Silva, *Ber.*, **6**, 35 (1873).

the same as the uncharacterized dichloride of Friedel and Silva.⁷ An attempt to hydrolyze 1,3-dichloro-2,3-dimethylbutane by refluxing it with a 10% solution of sodium carbonate for 36 hours was unsuccessful. This is similar to the results reported by Bergmann⁸ in the attempted hydrolysis of 1,3-dibromo-2,3-dimethylbutane using a 7.3% solution of potassium carbonate at reflux temperature for 30 hours.

The hydrolysis of a mixture of the monochlorides gave only 2,3-dimethyl-1,3-butadiene and 2,3-dimethyl-1-buten-3-ol. This is the same result reported by Tishchenko³ and Chupotsky and Maritzu⁴ on the hydrolysis of their monochloride. In a similar manner Bergmann⁸ and Claisen, *et al.*,⁹ obtained only 2,3-dimethyl-1-buten-3-ol by the hydrolysis of a monobromide which they characterized as 1-bromo-2,3-dimethyl-2-butene.

In view of the ease with which 1-chloro-2,3-dimethyl-2-butene and 3-chloro-2,3-dimethyl-1-butene undergo allylic rearrangement, it is suggested that the characterization of the corresponding bromides in the literature should be questioned.

1-Chloro-2,3-dimethyl-2-butene reacts with potassium iodide in acetone at 20° at a rate approximately 150 times faster than does allyl chloride,¹⁰ 100 times faster than methallyl chloride¹⁰ and 5 times faster than 1-chloro-3-methyl-2-butane.¹¹ A theory to explain this increase in reactivity with an increase in the replacement of hydrogen atoms by methyl groups (or other types of groups) will be presented in a subsequent paper.

1-Chloro-2,3-dimethyl-2-butene reacts completely with sodium ethoxide in ethanol within seven seconds at -70°. Apparently the reaction is predominately ionic in nature and shows the same great activation, caused by replacing both terminal hydrogen atoms by methyl groups, which was first noted with 1-chloro-3-methyl-2-butene.

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Experimental

2,3-Dimethyl-1,3-butadiene.—2,3-Dimethyl-1,3-butadiene was prepared from pinacol according to the procedure of Howard and co-workers⁵; b.p. 69.0° (745 mm.), n_D^{20} 1.4390, n_D^{25} 1.4361, n_D^{30} 1.4332, d_4^{20} 0.7265, d_4^{25} 0.7217, d_4^{30} 0.7169; lit.⁵ b.p. 68.5-71.5° (760 mm.); n_D^{20} 1.4388, d_4^{20} 0.7267.

Hydrochlorination of 2,3-Dimethyl-1,3-butadiene under Anhydrous Conditions.—The hydrochlorination was carried out by adapting the Howard⁵ method to a batch operation using a large test-tube fitted with a thermometer, stirrer and a bottom inlet for hydrogen chloride. The temperature of the hydrochlorination was measured by the ther-

(8) A. G. Bergmann, *J. Russ. Phys. Chem. Soc.*, **52**, 24 (1920); *C. A.*, **17**, 1420 (1923).

(9) L. Claisen, F. Kremers, F. Roth and E. Tietze, *J. prakt. Chem.*, [3] **105**, 65 (1922).

(10) L. F. Hatch, L. B. Gordon and J. J. Russ, *THIS JOURNAL*, **70**, 1093 (1948).

(11) L. F. Hatch and L. S. Gerhardt, *ibid.*, **71**, 1679 (1949).

meter immersed in the 2,3-dimethyl-1,3-butadiene and was regulated by the rate of addition of Dry Ice to the acetone-bath in which the reactor was held. Addition of hydrogen chloride was discontinued when the reaction mixture showed the desired gain in weight. The product was flash distilled under reduced pressure at a temperature below 10°, at which temperature rearrangement of the isomers is slow enough to be disregarded for the short periods of time involved in this distillation. The reaction mixture was analyzed both by refractive index and by infrared spectra. Table II shows the relationship between the reaction temperature and yield of 1-chloro-2,3-dimethyl-2-butene, the other product is 3-chloro-2,3-dimethyl-1-butene. Dichlorides were not formed during this reaction and it was not possible to prepare dichlorides by hydrochlorinating the monochlorides under these same conditions.

TABLE II

Reaction temp., °C.	1-Chloro-2,3-dimethyl-2-butene, %	
	By refractive index	By infrared spectra
-25	12.7	13.9
-47	14.0	15.9
-69	15.5	17.5

Howard and co-workers⁵ report a quantitative yield of 1-chloro-2,3-dimethyl-2-butene at -30°.

3-Chloro-2,3-dimethyl-1-butene.—The reaction mixture from the hydrochlorination reaction was fractionated at a pressure of 45 mm. through a four-foot column packed with 1/8 inch glass helices and fitted with a total reflux head. The distillate was collected at Dry Ice temperatures. The 3-chloro-2,3-dimethyl-1-butene was essentially free of the higher boiling 1-chloro-2,3-dimethyl-2-butene as shown by infrared spectra. Physical data for 3-chloro-2,3-dimethyl-1-butene are given in Table I.

*Anal.*¹² Calcd.: Cl, 29.91. Found: Cl, 29.83, 29.90.

1-Chloro-2,3-dimethyl-2-butene.—After removal of the 3-chloro-2,3-dimethyl-1-butene, the residue from the hydrochlorination mixture was repeatedly fractionated at a pressure of 1–2 mm. until successive fractionations resulted in no change in refractive index of the distillate. Physical data for 1-chloro-2,3-dimethyl-2-butene are given in Table I.

*Anal.*¹² Calcd.: Cl, 29.91. Found: Cl, 29.88, 29.88.

Hydrochlorination of 2,3-Dimethyl-1,3-butadiene under Aqueous Conditions.⁶—The following quantities of materials were shaken together for seven hours: concd. hydrochloric acid, 377.4 g. (3.8 moles), copper(I) chloride, 15.4 g. (0.078 mole), ammonium chloride, 6 g. (0.11 mole), 2,3-dimethyl-1,3-butadiene, 88 g. (1.08 moles). The organic phase was separated, washed with water, dried and distilled to yield a mixture of 1-chloro-2,3-dimethyl-2-butene, 3-chloro-2,3-dimethyl-1-butene, 1,3-dichloro-2,3-dimethylbutane (29%) and a small amount of 2,3-dichloro-2,3-dimethylbutane, m.p. (closed tube) 158–159°; lit.⁷ 159–160°. Physical data for 1,3-dichloro-2,3-dimethylbutane are given in Table I.

*Anal.*¹² Calcd.: Cl, 45.73. Found: Cl, 45.34, 45.40.

Ethyl Ester of 3-Hydroxy-2,3-dimethylbutanoic Acid.—This compound was prepared with a 57% yield by the Reformatsky condensation of ethyl α -bromopropionate and acetone in benzene with zinc; b.p. 72–74° (8 mm.); n_D^{20} 1.4289, n_D^{25} 1.4267, n_D^{30} 1.4244, d_4^{25} 0.9671; lit. b.p. 105° (30 mm.),¹³ 99° (28 mm.).¹⁴

2,3-Dimethyl-1,3-butanediol.—Ethyl 3-hydroxy-2,3-dimethylbutanoate (0.353 mole) was refluxed with 0.55 mole of lithium aluminum hydride in ether solution for one hour. Excess reducing agent was destroyed by the addition of ethyl acetate. After hydrolysis of the complex, the diol was extracted with ether. Distillation gave a heavy hygroscopic product for which physical data are given in Table I; yield 60%.

Anal. Calcd.: C, 60.97; H, 11.94. Found: C, 60.37; H, 11.93.

1,3-Dichloro-2,3-dimethylbutane from 2,3-Dimethyl-1,3-butanediol.—2,3-Dimethyl-1,3-butanediol (0.16 mole) was

refluxed for one hour with 0.35 mole of thionyl chloride containing 10 drops of pyridine. After washing with water and dilute sodium carbonate solution and drying over calcium chloride, the product was distilled; b.p. 82.5° (45 mm.), 160–161° (753 mm.), n_D^{20} 1.4507, d_4^{30} 1.059. The infrared spectrum of this material was essentially identical with that of the product prepared by hydrochlorination of 2,3-dimethyl-1,3-butadiene and of a mixture of the two monochlorides prepared during this investigation.

Hydrolysis of the Mixed Monochlorides.—Ten milliliters of the mixture of monochlorides (n_D^{20} 1.4455) was refluxed for six hours with 250 ml. of a 2.5% sodium carbonate solution. The odor of 2,3-dimethyl-1,3-butadiene was evident during this period. Extraction of the reaction mixture with ether followed by distillation gave 2.2 ml. of an alcohol; b.p. 117–119°. The literature gives the following boiling points (and ranges) for 2,3-dimethyl-1-buten-3-ol; 117.5–118°,⁴ 118–119°,⁹ 116.5–118°,⁸ 118°.¹⁵

Infrared Spectra.—The infrared spectra were determined using a Perkin-Elmer Model 12C spectrometer. Sodium chloride optics were used with a cell thickness of 0.025 mm. The absorption of the 1-chloro-2,3-dimethyl-2-butene at 8.1 μ was used in analysis of mixtures of the two monochlorides.

Following are the principal wave lengths in microns. The omission of the last figure in two cases represents a broad band.

1-Chloro-2,3-dimethyl-2-butene										
3.56	7.04	7.41	7.95	8.13	8.52	9.17	11.02	11.56	14	6
3-Chloro-2,3-dimethyl-1-butene										
3.42	6.16	6.99	7.35	8.65	9.11	11.14	13	55		
1,3-Dichloro-2,3-dimethylbutane										
3.50	6.99	7.40	7.77	7.99	8.07	8.53	9.00			
9.19	10.77	11.28	11.74	12.69	12.91	13.68				
3-Hydroxy-2,3-dimethylbutanoic acid ethyl ester										
3.09	3.47	5.92	6.95	7.38	7.57	8.05	8.6			
9.26	9.81	10.58	11.06	11.58	12.75	13.75				

Reaction of 1-Chloro-2,3-dimethyl-2-butene with Potassium Iodide in Acetone.—The procedure used was essentially the same as that previously described.¹⁰ It was necessary to extract the samples with carbon tetrachloride before titration to prevent fading of the end-points. The usual modified second-order equation, $k = 2.303/4 bt \log_{10} (5 - z)/5(1 - z)$, was used and a plot of $\log_{10} (5 - z)/5(1 - z)$ vs. time gave a straight line between 60 and 99% reacted. k calculated from this plot was 75.4.

TABLE III

REACTION WITH POTASSIUM IODIDE IN ACETONE AT 20°					
Time, hr.	0.10	0.15	0.20	0.25	0.30
% reacted	80.2	87.0	94.3	97.2	99.8
k , hr. ⁻¹ mole ⁻¹	82.9	70.8	76.3	77.0	69.6
Av. k	75.3 \pm 4.1				
Relative reactivity ^a	150				

^a Allyl chloride as 1.00 with $k = 0.502$; the usual $k = 0.218$ multiplied by 2.303, a conversion factor from \ln_{10} to \log_{10} which has been omitted in nearly all previous work.

Reaction of 1-Chloro-2,3-dimethyl-2-butene with Sodium Ethoxide in Ethanol.—The reaction with sodium ethoxide was so rapid as to render impossible the use of the usual procedure.¹⁶ Five-ml. samples of 0.1191 M sodium ethoxide and 0.0950 M 1-chloro-2,3-dimethyl-2-butene were cooled in a Dry Ice-acetone-bath. The samples were poured together and then immediately poured into water to stop the reaction. This procedure required about seven seconds. Titration of the resulting solution with hydrochloric acid indicated that the 1-chloro-2,3-dimethyl-2-butene had reacted quantitatively with the sodium ethoxide during this period.

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(12) E. Chablay, *Ann. chim.*, **1**, 510 (1914).

(13) W. H. Perkin, *J. Chem. Soc.*, **69**, 1457 (1896).

(14) J. C. Bardham, *ibid.*, 2604 (1928).

(15) A. Courtot, *Bull. soc. chim.*, [3] **35**, 978 (1906).

(16) L. F. Hatch and H. E. Alexander, *This Journal*, **71**, 1037 (1949).