showing that even large differences in the electronic properties of the migrating groups do not significantly influence the relative extents of migration. *o*-Toluanilide was the major product obtained from *o*-methylbenzophenone, as is also the case when this ketone is oximated and subjected to the Beckmann rearrangement.

ANN ARBOR, MICH. RECEIVED NOVEMBER 30, 1949

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

Allylic Chlorides. X. Configuration of the 3-Chloro-2-buten-1-ols and the 1,3-Dichloro-2-butenes

BY LEWIS F. HATCH AND PAUL S. HUDSON[1]

The recent preparation and study of the 1,3-dichloro-2-butenes has resulted in considerable information pertaining to these compounds and the corresponding chloroalcohols (3-chloro-2-buten-1-ol).[2] These data, however, furnish only indirect evidence as to the arrangement of atoms and groups around the carbon–carbon double bond, and the conclusion drawn as to the structure of the two isomers was based upon an assumption of structure for the two isomers of 1,3-dichloropropene which was subsequently shown to be incorrect.[3] The purpose of the present investigation was to obtain further evidence pertaining to the geometrical configuration of the 3-chloro-2-buten-1-ols (and indirectly, of the 1,3-dichloro-2-butenes).

Previous work with the 3-chloro-2-propen-1-ols has shown that the isomer with the chlorine and hydrogen atoms *trans* to one another will dehydrochlorinate more readily than when they are in the *cis* position.[4] This behavior is in keeping with the generally accepted theory of the relative ease of *trans* elimination.[5] This same reaction, therefore, should be useful in elucidating the structure of the 3-chloro-2-buten-1-ols.

The results of the dehydrochlorination of both isomers of 3-chloro-2-buten-1-ol are given in Table I. It was not possible to determine accurately the purity of the *beta* isomer, but it is thought to be substantially *beta*-3-chloro-2-buten-1-ol.

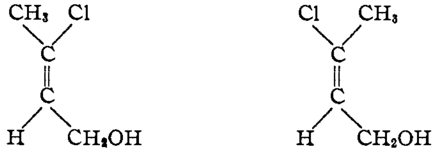
TABLE I

DEHYDROCHLORINATION OF 3-CHLORO-2-BUTEN-1-OL

Run	Isomer	Time, hr.	NaOH, %	Reflux temp., °C.	Reacted (from Cl^-), %
1	α	2	0.0	98.2	0.4
2	α	2	1.0	98.4	14.6
3	α	2	2.5	98.9	25.5
4	α	2	5.0	99.6	28.8
5	α	2	10.0	100.7	32.0
6	α	2	20.0	105.7	39.0
7	α	2	30.0	111.8	51.5
8	α	2	40.0	115.0	56.6
9	α	2	50.0	134.5	66.5
10	α	0.5	30.0	111.8	29.2
11	α	1	30.0	111.8	40.3
12	α	2	30.0	111.8	51.1
13	α	3	30.0	111.8	55.6
14	α	4	30.0	111.8	59.3
15	α	6	30.0	111.8	60.4
1	β	2	5	100.3	23.2
2	β	2	10	101.3	27.2
3	β	2	20	106.4	36.7
4	β	2	30	112.5	45.6
5	β	2	40	115.7	54.6
6	β	1	30	112.5	34.7
7	β	3	30	112.5	47.8
8	β	4	30	112.5	49.5
9	β	6	30	112.5	50.5

These data show that under varying conditions of time and concentration of sodium hydroxide solution the α-3-chloro-2-buten-1-ol dehydrochlorinates more readily. While the difference in the degree of reactivity is not so great as with previously reported geometrical isomers, the difference is a real one. The magnitude of difference in reactivity is not so significant as the fact that there is a difference. It is probable that because the β-3-chloro-2-buten-1-ol is thermally less stable than the α-isomer, partial rearrangement to the more reactive α-isomer occurs during the dehydrochlorination reaction. It is also possible, but not too probable, that the rate at which the chloroalcohols dissolve in the basic aqueous medium is the controlling factor in respect to the rate of reaction.

Because the α-isomer is more reactive than the β-isomer it follows that the α-isomer has the chlorine atom *trans* to the hydrogen atom.



α- β-

3-Chloro-2-buten-1-ol

α-3-Chloro-2-buten-1-ol is produced from α-1,3-dichloro-2-butene and the α-dichloride can be regenerated from the α-chloroalcohol.[2] The β-

---

[1] Department of Chemistry, Cornell College, Mount Vernon, Iowa.

[2] Hatch and Ballin, THIS JOURNAL, **71**, 1039, 1041 (1949).

[3] Hatch and Perry, *ibid.*, **71**, 3262 (1949).

[4] Hatch and Moore, *ibid.*, **66**, 285 (1944).

[5] (a) Michael, *J. prakt. Chem.*, [2] **52**, 289 (1895); (b) Michael, THIS JOURNAL, **40**, 704, 1674 (1918); (c) Wislicenus and Schmidt, *Ann.*, **313**, 216 (1900); (d) Chavanne, *Compt. rend.*, **154**, 776 (1912).

isomers undergo similar reactions. Because of these relationships, it is assumed that the α-dichloride has the same configuration as the *alpha* chloroalcohol and that the β-isomers of these compounds are related in structure in a similar manner.[6]

The designation *cis* and *trans* with respect to configuration is purely arbitrary when applied to geometrical isomers with four different groups around the carbon–carbon double bond and will not be used with these compounds.

The dehydrochlorination of the readily available 3-chloro-2-buten-1-ol provides a desirable method for the production of 2-butyn-1-ol. Although the conversions are not high, the procedure is more convenient than those previously reported[7] and the yields are high. The conversions can be increased appreciably by the use of alcoholic alkali instead of aqueous alkali.

Experimental

α-1,3-Dichloro-2-butene.—The α-1,3-dichloro-2-butene was obtained by distillation of DCB[8] (1,3-dichloro-2-butene). A center cut had the following constants: b. p. 127.8° (745 mm); $n^{25}\mathrm{D}$ 1.4695; $d^{25}{}_4$ 1.1528 (lit.[2] b. p. 127.9°; $n^{25}\mathrm{D}$ 1.4695; $d^{25}{}_4$ 1.1528).

α-3-Chloro-2-buten-1-ol.—The α-3-chloro-2-buten-1-ol was obtained in a 69% yield from α-1,3-dichloro-2-butene by hydrolysis using a 4% solution of sodium carbonate and a temperature of 80° (time, three hours).[2] A center cut of the distilled product had the following constants: b. p. 160.5° (747 mm.); $n^{25}\mathrm{D}$ 1.4635; $d^{25}{}_4$ 1.1064 (lit.[2] b. p. 164.0° [161–162°][9]; $n^{25}\mathrm{D}$ 1.4630; $d^{25}{}_4$ 1.1058).

Dehydrochlorination of α-3-Chloro-2-buten-1-ol.—This chloroalcohol was dehydrochlorinated using various concentrations of aqueous sodium hydroxide and for various periods of time with the same concentration of sodium hydroxide solution. The following is a description of a *typical run*.

Ten and seven-tenths grams (0.1 mole) of the chloroalcohol and 13.3 g. (0.1 mole) of sodium hydroxide as a 30% solution were placed in a 200-ml. round-bottom flask fitted with a reflux condenser and the mixture was allowed to reflux for two hours. The reflux temperature varied from 98.2° for 1% sodium hydroxide solution to 134.5° for a 50% sodium hydroxide solution. After two hours the reaction mixture was neutralized with dilute nitric acid and the organic material distilled as an azeotrope. No attempt was made to recover 2-butyn-1-ol from the azeotrope because of the small quantities of material involved in the reaction. The remaining solution in the reaction flask was filtered through a Buchner funnel. To this clear filtrate solid silver nitrate was added in excess to cause the complete precipitation of silver chloride. The extent of reaction was determined by the amount of chloride ion formed as indicated by the precipitated silver chloride. The data are given in Table I.

β-1,3-Dichloro-2-butene.—β-1,3-Dichloro-2-butene was prepared in an 86% yield from freshly distilled chloroprene[8] and concentrated hydrochloric acid in the presence of copper(I) chloride and ammonium chloride at room temperature.[2] The organic layer of the reaction mixture was separated and washed with 50-ml. portions of water, 10% solution of sodium hydrogen carbonate and again with water. The organic material was dried over magnesium sulfate during which time the unreacted chloroprene polymerized. The dried material was filtered and its boiling point (131° at 748 mm.) and index of refraction ($n^{25}\mathrm{D}$ 1.4705) indicated that it was substantially β-1,3-dichloro-2-butene (lit.[2] b. p. 129.9°; $n^{25}\mathrm{D}$ 1.4711).

β-3-Chloro-2-buten-1-ol.—One hundred and twenty-five grams (1.0 mole) of the crude β-1,3-dichloro-2-butene was treated with 106 g. (1.0 mole) of sodium carbonate (as a 4% solution) in a three liter three necked flask equipped with mercury sealed stirrer and a reflux condenser. After two hours at 70° the mixture was then saturated with sodium chloride. The organic layer (71.5 g.) was separated and dried over sodium sulfate. The dried product was placed in a 250 ml. filter flask and 13 g. of material was "flashed" off at a pressure of 1 mm. The remaining material (58.5 g.—55% yield) had the following constants: b. p. 164° (747 mm.); $n^{25}\mathrm{D}$ 1.4655; $d^{25}{}_4$ 1.1094 (lit.[2] b. p. 166; $n^{25}\mathrm{D}$ 1.4653; $d^{25}{}_4$ 1.1085).

This material was assumed to be substantially the β-isomer of 3-chloro-2-buten-1-ol. It may have contained a small amount of unreacted 1,3-dichloro-2-butene and the expected ether.

Dehydrochlorination of β-3-Chloro-2-buten-1-ol.—β-3-Chloro-2-buten-1-ol was dehydrochlorinated using various concentrations of aqueous sodium hydroxide and for various periods of time in a manner similar to that used for the α-isomer. The data are recorded in Table I.

Preparation of 2-Butyn-1-ol.—One hundred and six and six-tenths grams (1.0 mole) of α-3-chloro-2-buten-1-ol and 40 g. (1.0 mole) of sodium hydroxide as a 30% solution were placed in a one-liter round-bottom flask fitted with a reflux condenser and the mixture was allowed to reflux for two hours. The reaction mixture was then cooled, neutralized with dilute hydrochloric acid and the organic material removed by distillation as its azeotrope with water. The azeotrope was worked up in the usual manner and dried. Distillation through a four-foot glass-helix packed column at atmospheric pressure (748 mm.) gave a 40% yield of 2-butyn-1-ol with no attempt made to recover the unreacted chloroalcohol. The 2-butyn-1-ol had the following constants: b. p. 141–142°; $n^{25}\mathrm{D}$ 1.4510; $d^{25}{}_4$ 0.9315; *MR* (calcd.) 20.20, (obsd.) 20.21 (lit.[10] b. p. 141–143°; $n^{21}\mathrm{D}$ 1.453; d^{21} 0.958).

Summary

The difference in rate of dehydrochlorination has been used to assign configuration to the two isomers (α and β) of 3-chloro-2-buten-1-ol and, indirectly, of 1,3-dichloro-2-butene.

The low boiling isomer (α) of 3-chloro-2-buten-1-ol dehydrochlorinates more readily than the β isomer and because of this fact the α isomer has been assigned the structure with the chlorine and hydrogen atoms in the *trans* position in respect to the carbon–carbon double bond.

The high boiling isomer of both the chloroalcohol and the dichloride are assigned the configuration in which the chlorine atom and the hydrogen atom are in the *cis* position.

2-Butyn-1-ol has been prepared by the dehydrochlorination of 3-chloro-2-buten-1-ol.

AUSTIN, TEXAS RECEIVED SEPTEMBER 30, 1949

---

[6] This assignment of configuration has been partially confirmed by the replacement of the allylic chlorine atom of α-1,3-dichloro-2-butene by a hydrogen atom using lithium aluminum hydride to give *trans*-2-chloro-2-butene. Private communication from Robert H. Perry, Jr.

[7] (a) Zal'kind and Gverdtsiteli, *J. Gen. Chem.* (*U. S. S. R.*), **9**, 971 (1939); *C. A.*, **33**, 8570 (1939); (b) Guest, THIS JOURNAL, **47**, 860 (1925). (c) Tchao Yin Lai, *Bull. soc. chim.*, **53**, 682 (1933).

[8] Furnished for this research by E. I. du Pont de Nemours & Co., Wilmington, Delaware.

[9] Petrov, *J. Gen. Chem.* (*U. S. S. R.*), **10**, 1418 (1940).

[10] Yvon, *Compt. rend.*, **180**, 748 (1925).