amount of hydrogen was taken up. The product, 1,2-diphenylethane, was isolated easily in crystalline form by dilution of the solvent with water. In this case, both oxygenated functional groups were converted to methylene groups.

Acknowledgment.—We are indebted to the Research Corporation for a grant-in-aid of this work.

Experimental

All melting points are corrected.

Palladium–Carbon Catalyst.—A 5% palladium–carbon catalyst was prepared according to the general method of Hartung.[5] The palladium was obtained from J. Bishop and Company, in a 10% solution, and was deposited on Norit.

γ-(*p*-Tolyl)-butyric Acid.—A mixture of 20.0 g. of β-(*p*-toluyl)-propionic acid,[6] 3.0 g. of 5% palladium–carbon catalyst, and 40 ml. of acetic acid was shaken with hydrogen (initial pressure, 40 lb.) in a Parr hydrogenation apparatus at approximately 65°. The reduction (100% absorption) was completed in about twenty-five minutes. No further absorption occurred on continued shaking. The catalyst was removed by filtration and washed with acetic acid. The solvent was removed by distillation at atmospheric pressure; the distillation was continued under reduced pressure to yield 14.7 g. (79%) of γ-(*p*-tolyl)-butyric acid, b. p. 124–134° (0.3–0.5 mm.), m. p. 54–56° (reported, m. p. 61–62°, 92%, Clemmensen–Martin method).[7]

γ-(*p*-Anisyl)-butyric Acid.—The reduction of 20.8 g. of β-(*p*-anisoyl)-propionic acid[8] was carried out in 125 ml. of acetic acid with 3.0 g. of 5% palladium–carbon catalyst at approximately 65°. About forty minutes was required for the reduction (100% absorption). After removal of the catalyst, the solution was added to 200 ml. of water. The mixture was chilled and filtered to provide 14.5 g. (75%) of colorless γ-(*p*-anisyl)-butyric acid, m. p. 61–62° (reported, Clemmensen–Martin method, m. p. 59–60°, 65%[9]; m. p. 60–61°, 85%[7]; Wolff–Kishner–Huang method, 75%.[10]

***o*-Benzylbenzoic Acid.**—The reduction of 27.6 g. of *o*-benzoylbenzoic acid was carried out in 40 ml. of acetic acid with 3.0 g. of palladium–carbon catalyst at approximately 65°. About seventy-five minutes was required for completion of the reaction. After removal of the catalyst, the solution was poured into 200 ml. of water, and the mixture chilled for twelve hours. Filtration and drying *in vacuo* yielded 24.5 g. (95%) of colorless *o*-benzylbenzoic acid, m. p. 111–113° (reported, m. p. 113–114.2°, 75%, Clemmensen method).[11] The product was completely soluble in warm sodium bicarbonate solution.

1,2-Diphenylethane.—The reduction of 21.2 g. of benzoin was carried out in 200 ml. of acetic acid with 3.0 g. of 5% palladium–carbon catalyst at 65°; the rate of hydrogen absorption slowed gradually and stopped after about eight hours at 92% of completion. The catalyst was removed and the solution was poured into 300 ml. of water. The product crystallized immediately; after chilling, filtration yielded 13.5 g. (74%) of 1,2-diphenylethane, m. p. 49–50° (reported,[12] 51.5–52.5°).

Summary

A method for the catalytic reduction of certain aryl ketones is described. The keto group is reduced to a methylene group in acetic acid solution at 65° with a palladium–carbon catalyst.

PHILADELPHIA 4, PENNSYLVANIA

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[5] "Organic Syntheses," **26**, 77 (1946).

[6] "Organic Syntheses," Coll. Vol. II, 82 (1943).

[7] Martin, THIS JOURNAL, **58**, 1438 (1936).

[8] Fieser and Hershberg, *ibid.*, **58**, 2314 (1936).

[9] Fieser, *et al.*, *ibid.*, **70**, 3200 (1948).

[10] Dauben and Adams, *ibid.*, **70**, 1759 (1948).

[11] Bradlow and VanderWerf, *ibid.*, **69**, 1254 (1947).

[12] Cannizzaro and Rossi, *Ann.*, **121**, 251 (1862).

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

Allylic Chlorides. V. Relative Reactivities with Sodium Ethoxide in Ethanol

BY LEWIS F. HATCH AND HAROLD E. ALEXANDER

The relative reactivities of various allylic chlorides with potassium iodide in acetone have been reported[1,2] which indicate that both position isomerism and geometrical configuration have an effect on the rate of reaction. Although the reaction between sodium ethoxide and several allylic chlorides has been reported,[1,3] no effort had been made to ascertain if this reaction is influenced by geometrical configuration until the recent work of Andrews and Kepner.[4] Young and Andrews[3] had, however, suggested that this might be the case.

The present study was made to extend previously reported investigations on the sodium ethoxide reaction to determine the effects of substituents on the rate of reaction, and also to confirm the observation of Andrews and Kepner pertaining to the lack of influence of geometrical isomerism.

Materials

1-Chloro-1-propene.—A mixture of *cis* and *trans* 1-chloro-1-propene (Research Chemicals, San Jose, California) was distilled to obtain a fraction with a boiling range of 34–35°. This fraction, being intermediate in boiling range between the two isomers (*cis* 32.0–32.2°; *trans* 36.7°), was assumed to contain both isomers.

Allyl chloride[5] boiling at 44.3° was used without further purification; $n^{25}\mathrm{D}$ 1.4109.

Methallyl chloride[5] was redistilled and a fraction boiling at 70.9–71.0° was used.

2-Bromo-3-chloro-1-propene obtained from Halogen Chemicals of Columbia, S. C., was distilled at 150 mm. pressure. The fraction used boiled at 61.5°; $n^{25}\mathrm{D}$ 1.4967.

2,3-Dichloro-1-propene[5] was distilled at 150 mm. pressure and a fraction boiling at 48° was used: $n^{25}\mathrm{D}$ 1.4578; d^{25}_{4} 1.2004; *MR* (calcd.) 25.32, (obsd.) 25.16.

1,3-Dichloropropene.—A mixture of the two isomers of 1,3-dichloropropene[5] was fractionated. The low boiling

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[1] Tamele, Ott, Marple and Hearne, *Ind. Eng. Chem.*, **33**, 115 (1941).

[2] Hatch, Gordon and Russ, THIS JOURNAL, **70**, 1093 (1948).

[3] Young and Andrews, *ibid.*, **66**, 421 (1944).

[4] Andrews and Kepner, *ibid.*, **70**, 3456 (1948).

[5] Furnished by Shell Chemical Co., San Francisco, California.

isomer boiled at 103.3°: $n^{25}D$ 1.4653. The high boiling isomer boiled at 111.5–111.9°: $n^{20}D$ 1.4742.

1,3-Dichloro-2-methyl-1-propene.—The isomeric 1,3-dichloro-2-methyl-1-propenes were prepared from methallyl chloride.[6] The methallyl chloride was chlorinated to 1,2,3-trichloro-2-methylpropane using sulfuryl chloride. The trichloride was dehydrochlorinated and hydrolyzed to a mixture of the 3-chloro-2-methyl-2-propen-1-ols from which the two alcohols were separated by means of a Podbielniak Hypercal distillation column. The chloroalcohols were converted to the corresponding dichlorides using concentrated hydrochloric acid. The low boiling isomer boiled at 130°: $n^{25}D$ 1.4702. The high boiling isomer boiled at 132°: $n^{25}D$ 1.4745.

1,1,3-Trichloro-2-methyl-1-propene was obtained from Halogen and Perfume Chemicals, Columbia, S. C., and was distilled at 150 mm. The fraction used boiled at 101°: $n^{25}D$ 1.4932.

Experimental

The rates of reaction were obtained at 50.0 ± 0.1° using the procedure described by Tamele, *et al.*[1] The molar concentration of the chloride was 0.0998 ± 0.0018 and of the sodium ethoxide 0.0984. The data obtained are given in Table I. For each chloride at least four measurements were made covering the range of about 25 to 60% conversion. The individual values showed little or no drift and were constant as indicated in column 3 of Table I wherein the mean values of *k* are given along with the average deviation of the individual measurements from them.

Discussion

Table I lists the various allylic chlorides studied in the increasing order of their relative reactivity. The rate constant of allyl chloride was taken as unity, because all the other allylic chlorides may be considered as derivatives of allyl chloride, and also for a comparison between this reaction and that with potassium iodide.[2] A mixture of *cis* and *trans* 1-chloro-1-propene was tested to determine if a vinyl chlorine would react under the conditions of the rate determinations. There was no measurable reaction in twenty-four hours at 50°.

TABLE I

RELATIVE REACTIVITIES OF ALLYLIC CHLORIDES

Compound	*k* for $NaOC_2H_5$ 50°	Rel. reactivity $NaOC_2H_5$ 50°	KI 20°[a]
$CHCl{=}CH{-}CH_3$[b]	0.00	0.00	0.00
$CH_2{=}CCl{-}CH_2Cl$	0.56 ± 0.005	0.47	0.72
$CH_2{=}CBr{-}CH_2Cl$	0.97 ± 0.06	0.82	0.87
$CH_2{=}CH{-}CH_2Cl$	1.18 ± 0.01	1.00	1.00
$CH_2{=}C(CH_3){-}CH_2Cl$	1.22 ± 0.03	1.03	1.58
$CHCl{=}CH{-}CH_2Cl$[d]	3.28 ± 0.06	2.78	8.58
$CHCl{=}CH{-}CH_2Cl$[e]	4.10 ± 0.06	3.47	2.90
$CHCl{=}C(CH_3){-}CH_2Cl$[d]	3.11 ± 0.13	2.64	32.8
$CHCl{=}C(CH_3){-}CH_2Cl$[e]	3.22 ± 0.11	2.73	8.45
$CCl_2{=}C(CH_3){-}CH_2Cl$	8.75 ± 0.15	7.42	33
$CH_3CH{=}CH{-}CH_2Cl$[c]		3.71[c]	2.37[c]

[a] Hatch, Gordon and Russ, THIS JOURNAL, **70**, 1093 (1948). [b] A mixture of *cis* and *trans* isomers. [c] Tamele, Ott, Marple and Hearne, *Ind. Eng. Chem.*, **33**, 115 (1941). This may be the *trans* isomer. [d] Low boiling. [e] High boiling.

The influence of the relative electronegativity the atom or group on the number 2 carbon apparently is not as pronounced nor as consistent as it is for the reaction with potassium iodide. The effect of replacing the number 2 hydrogen with chlorine is more pronounced than in the potassium iodide reaction, but the bromine compound has essentially the same relative reactivity. Replacing the hydrogen with a methyl group increases the reactivity very slightly in contrast to a definite increase in reactivity toward potassium iodide. There is a slight inhibiting effect of the methyl group noted between the 1,3-dichloropropenes and the 1,3-dichloro-2-methyl-1-propenes.

A chlorine atom on the number 1 carbon causes a definite increase in the reaction rate, while a second chlorine atom in the same position (1,1,3-trichloro-2-methyl-1-propene) more than doubles the relative reactivity. Tamele, *et al.*, found that crotyl chloride (probably either *trans* or predominantly *trans*) had a relative reactivity of 3.71 at 35° compared to allyl chloride at the same temperature. This would indicate that a methyl group on the number 1 carbon has a greater activating effect than chlorine in the same position. Previous work[1,2] has indicated that with potassium iodide, chlorine has a greater activating effect than a methyl group.

The effect of geometrical configuration is much less pronounced and in the opposite direction from that shown in the reaction with potassium iodide. It is of interest to note that the high boiling isomer of 1,3-dichloropropene has nearly the same relative reactivity for both reactions. The relative reactivities of both isomers of 1,3-dichloro-2-methyl-1-propene, however, are much less than with potassium iodide. This reduced reactivity with sodium ethoxide may be caused by the lack of the activating effect of a methyl group in the number 2 position, an activation which is present with the potassium iodide reaction.

From these observations it is suggested that the reactions of allylic chlorides with sodium ethoxide and with potassium iodide may go by different mechanisms. It has been postulated[2] that the reaction with potassium iodide takes place through a negative iodide ion attack on the carbon atom holding the allylic chlorine. It may be that the reaction with sodium ethoxide is through an electrophilic attack on the allylic chlorine by the sodium ethoxide molecule. A reaction of this type should not be influenced appreciably by geometrical configuration, but should respond to inductive effects.

Acknowledgment.—This investigation was supported by a Grant-in-Aid from the Research Corporation for "Research on Allylic Chlorides." The authors wish to express their appreciation.

Summary

A study has been made of the effect of both substituents and geometrical configuration on the relative reactivity of allylic chlorides with sodium ethoxide in ethanol at 50°.

Hatch, Russ and Gordon, THIS JOURNAL, **69**, 2614 (1947).

The replacement of the hydrogen on the number 2 carbon by chlorine or bromine decreases the reactivity of the allylic chlorine. The effect of a methyl group in this position is very slight.

The replacement of the hydrogen on the number 1 carbon by chlorine causes a marked increase in reactivity.

It has been confirmed that geometrical configuration has only a slight effect on this reaction. It is suggested that the reaction mechanism for the reaction with sodium ethoxide is different from that in the reaction between allylic chlorides and potassium iodide.

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

Allylic Chlorides. VI. Preparation of the 1,3-Dichloro-2-butenes

BY LEWIS F. HATCH AND STUART G. BALLIN

Several investigators have reported the preparation of 1,3-dichloro-2-butene from either vinylacetylene[1,2] or methyl vinyl ketone,[3] but no attempt was reported of the isolation and characterization of its two geometrical isomers. This is understandable, because the two isomers boil within 2 degrees of one another, and the higher boiling isomer rearranges to the lower boiling isomer rather readily.

Recently, 1,3-dichloro-2-butene has become available commercially and is called DCB.[4] It was possible, however, to obtain only the lower boiling isomer from this material probably because previous heating had rearranged the higher boiling isomer to the lower.

The two isomers of 1,3-dichloro-2-butene have now been prepared by the addition of hydrogen chloride to chloroprene. The isomers have been separated and various physical constants obtained. The same constants were also obtained for the corresponding isomeric chloro-alcohols (3-chloro-2-buten-1-ol). These data, together with available data from the literature, are given in Table I.

The 3,5-dinitrobenzoates were prepared from the dichlorides by use of silver 3,5-dinitrobenzoate and from the chloro-alcohols using 3,5-dinitrobenzoyl chloride. The high boiling chloro-alcohol gave a derivative of each isomer, probably because the hydrogen chloride (produced in the reaction) brought about interconversion.[5] This interconversion was also observed in the regeneration of the dichlorides from the corresponding chloro-alcohols. These interconversions of the high boiling isomer to the low boiling isomer would indicate that the high boiling isomer had the *cis* configuration. The geometrical configuration of the two isomers as indicated by their relative reactivities with potassium iodide,[6] cuprous chloride catalyzed hydrolysis[7] and sodium ethoxide[8] is discussed in the following paper.[9]

Experimental

Attempt to Obtain the Geometrical Isomers of 1,3-Dichloro-2-butene from Commercial Sources.—Only the low boiling isomer of 1,3-dichloro-2-butenes ($n^{25}\mathrm{D}$ 1.4695) was isolated from DCB[4] by distillation at various pressures down to 20 mm.

Hydrochlorination of Chloroprene.—Two moles of chloroprene distilled from a chloroprene solution[10] containing 50% xylene and 0.1% catechol by weight was shaken for twelve hours in a pressure bottle at room temperature with 37% hydrochloric acid (4 moles), 50 g. of cuprous chloride, and 20 g. of ammonium chloride. The reaction mixture was then cooled and the organic layer was separated and distilled at 20 mm. pressure through a 40-cm. vacuum-jacketed column without packing. A 58% yield of relatively pure high boiling 1,3-dichloro-2-butene ($n^{25}\mathrm{D}$ 1.4708 to 1.4712) was obtained together with some unreacted chloroprene and polymers. Repeated distillations of the center cut at 20 mm. pressure caused no change in the refractive index of $n^{25}\mathrm{D}$ 1.4711 if the kettle temperatures were no higher than 35–40°.

Attempts to cause hydrogen chloride to add to chloroprene at room temperature without the use of cuprous chloride or under anhydrous conditions were unsuccessful.

Separation of the Isomeric 1,3-Dichloro-2-butenes.—When the products from the hydrochlorination of chloroprene were distilled through a 4-ft. glass-helices packed column at atmospheric pressure with kettle temperatures in the range of 130–135° a 30–40% yield of relatively pure low boiling 1,3-dichloro-2-butene ($n^{25}\mathrm{D}$ 1.4692–1.4699) was obtained. Further distillations at pressures of 1 atmosphere or less caused no further change in the refractive index of $n^{25}\mathrm{D}$ 1.4695. Moreover, when the higher boiling isomer was distilled at atmospheric pressure, or even at pressures of 150 and 100 mm., only the lower boiling isomer could be obtained in appreciable quantities.

Apparently the high boiling isomer is the labile form and can readily be converted to the stable isomer by heat. Attempts to demonstrate this by maintaining the two isomers at 100° were unsuccessful primarily because polymerization occurred with both isomers, and the resulting products could not be identified. The rate of polymerization of the high boiling isomer exceeded that of the low boiling isomer, as indicated by changes in index of refraction.

Small quantities of each isomer were stored in dark bottles at 0° and at 27° for five months; no change of the index of refraction was observed, but a discoloration developed in each case.

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(1) Carothers, Collins and Berchet, THIS JOURNAL, **54**, 4066 (1932).

(2) Carothers and Collins, U. S. Patent 2,102,611.

(3) Churbakov, *J. Gen. Chem.* (*U. S. S. R.*), **10**, 977 (1940).

(4) From E. I. du Pont de Nemours & Co., Wilmington, Delaware.

(5) Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943, p. 454.

(6) Hatch, Gordon and Russ, THIS JOURNAL, **70**, 1093 (1948).

(7) Hatch and Roberts, *ibid.*, **68**, 1196 (1946).

(8) Hatch and Alexander, *ibid.*, **71**, 1037 (1949).

(9) Hatch and Ballin, *ibid.*, **71**, 1041 (1949).

(10) Commercial grade of chloroprene solution was furnished us for this work by the du Pont de Nemours Co., Wilmington, Delaware.