ml. of ether was added a solution of 17.3 g. (0.10 mole) of 2-ethoxyquinoline in ether. The suspension turned from black to white during the 48-hour stirring time. The mixture was hydrolyzed with a solution of ammonium chloride and ammonium hydroxide. The ether layer was dried over sodium sulfate and the ether removed by distillation. The residue was distilled to yield 16.1 g. (93.2% recovery) of 2-ethoxyquinoline (b.p. 81–83° at 0.05 mm.).

Phenyllithium and 4,7-Dichloroquinoline.—A solution of 0.10 mole of phenyllithium in 100 ml. of ether was added dropwise at 0° to 19.8 g. (0.10 mole) of 4,7-dichloroquinoline in 300 ml. of ether. After stirring for 1 hour a yellow precipitate had formed and a Color Test I was negative. After hydrolysis with water the layers were separated and the ether layer dried over sodium sulfate. The ether was replaced with 400 ml. of anhydrous ethanol and 30 g. of mercuric oxide was added. After keeping this mixture just below the boiling point for 18 hours the mercury and mercuric oxide were removed by filtration. On cooling this solution yielded 19.6 g. of product (m.p. 100.5–101.5°). Concentration of mother liquors yielded 4.3 g., or a total of 23.2 g. (84.9%) of 2-phenyl-4,7-dichloroquinoline.[12] Recrystallized from ethanol the compound melted at 101–102°.

Phenyllithium and 2-Phenyl-4,7-dichloroquinoline.—A solution of 0.05 mole of phenyllithium[17] was added to a suspension of 13.7 g. (0.05 mole) of 2-phenyl-4,7-dichloroquinoline in 200 ml. of ether at 0° (bath temperature). The mixture turned black and gave no Color Test I[2] at the end of 1 hour. The suspension was poured into a slush of ether and Dry Ice and after warming to room temperature was hydrolyzed with 100 ml. of water. This was a mixture of substances which resisted all attempts at separation by fractional crystallization.

The reaction was repeated between −50° and room temperature for 12 hours, and a precipitate was obtained after hydrolysis. Chromatographic adsorption effected some separation but the small amounts of material obtained were not pure enough to analyze.

Summary

1. 2-Electronegatively substituted quinolines have been cleaved by *n*-butyllithium, phenyllithium and phenylmagnesium bromide to form 2-aryl- or alkylquinolines.

2. Of these three organometallic compounds phenyllithium gives the highest yields of cleavage products. Because it is more reactive, *n*-butyllithium causes more extensive side reactions. Phenylcadmium chloride does not effect the cleavage reaction.

3. The electronegative groups which have been cleaved from the 2-position of quinoline are Cl–, $CH_3C_6H_4S$–, C_6H_5O–, C_2H_5O–, C_3H_5O–, $C_6H_5CH_2O$– and $C_5H_{10}N$–.

AMES, IOWA RECEIVED JUNE 26, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA]

Allylic Rearrangements. XXIX. Relative Tendencies of Nucleophilic Substitution in Organic Halides

BY IRVING D. WEBB[1] AND WILLIAM G. YOUNG

In the dual mechanism hypothesis of nucleophilic substitution at a saturated carbon atom[2,3] the tendencies of various alkyl halides to undergo the S_N2 reaction decrease in the order methyl, ethyl, isopropyl, *t*-butyl, while the tendencies to undergo the S_N1 reaction increase in the same order. Frequently reaction conditions are such that both mechanisms take place in a given substitution reaction, notably so with isopropyl halides. It is generally believed that in an S_N2 reaction the nucleophilic agent attacks the tetrahedral carbon atom opposite the position from which a group is leaving. The decrease in S_N2 tendency in the series methyl to *t*-butyl has been attributed to an increase in steric hindrance to "back-side" attack on carbon by the nucleophile.[4] The decrease in reactivity to S_N2 in this series has also been attributed partially to a decrease in the attraction of carbon substituted with alkyl groups for the nucleophilic agent, due to electron release by the alkyl groups.[2,5]

However, this latter hypothesis appears not to be general. After completion of the present work[1] in 1944, Evans[4c] reached the same conclusion by considering the evidence of Hughes[6] and of Young and Andrews.[7] There followed an exchange of publications[8] concerned with the relative importance of polar effects and steric effects in substitution reactions. If we interpret Hughes and Ingold[8a] correctly, they would expect a retarding effect on alkyl groups on the rate (bimolecular) of reaction of alkyl halides with halide or ethoxide ions in ethanol. However, they have pointed out that exceptions to the stated effect on the bimolecular mechanism sometimes arise in the neighborhood of the bimolecular–unimolecular transition region.[9]

In the case of allylic systems[1] the effect of alkyl groups is clearly one of acceleration. Thus an increase in the rate of bimolecular substitution with an increase in electron accession at the seat of substitution is clearly demonstrated by the marked increases in second order rate constants as the hydrogens in the gamma position of allylic halides are replaced with alkyl groups. With these gamma-substituted allylic halides steric

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(1) The contents of this paper were taken from a thesis presented by Irving D. Webb for the degree of Ph.D., June 24, 1944.

(2) Hughes, *J. Chem. Soc.*, 968 (1946).

(3) Roberts, Young and Winstein, THIS JOURNAL, **64**, 2157 (1942).

(4) (a) Bergmann, Polanyi and Szabo, *Z. physik. Chem.*, **20B**, 162 (1933); (b) Bartlett and Rosen, THIS JOURNAL, **64**, 543 (1942); (c) Evans, *Nature*, **157**, 438 (1946).

(5) (a) Hughes and Ingold, *J. Chem. Soc.*, 244 (1935); (b) Catchpole, Hughes and Ingold, *ibid.*, 15 (1948).

(6) Hughes, *Trans. Faraday Soc.*, **37**, 603 (1941).

(7) Young and Andrews, THIS JOURNAL, **66**, 421 (1944).

(8) (a) Hughes and Ingold, *Nature*, **158**, 94 (1946); (b) Evans, *Trans. Faraday Soc.*, **42**, 719 (1946); (c) Evans, "The Reactions of Organic Halides in Solutions," Manchester University Press, 1940; (d) Evans, *Nature*, **158**, 586 (1946); (e) Evans, *ibid.*, **159**, 166 (1947); (f) Evans, *J. Chem. Soc.*, 558 (1947); (g) Hughes and Ingold, *Nature*, **159**, 166 (1947); (h) Dostrovsky, Hughes and Ingold, *J. Chem. Soc.*, 1283 (1948).

(9) (a) Hughes, *Trans. Faraday Soc.*, **37**, 609 (1941); (b) Hughes, Ingold and Shapiro, *J. Chem. Soc.*, 228 (1936).

effects are removed at least to such an extent that the effects of electron accession at the seat of substitution can be observed. For example as summarized in Table I, the rate of reaction of γ-methyl-γ-ethylallyl chloride (this paper) with ethoxide ion in ethanol is about five times that of γ-methylallyl (crotyl) chloride[3,10] which in turn is about four times that of allyl chloride.[10] Similarly crotyl bromide is about four times as reactive as allyl bromide,[11] and crotyl chloride about twice as reactive as allyl chloride[10] toward potassium iodide in acetone.

TABLE I

SECOND ORDER VELOCITY CONSTANTS FOR REACTIONS OF ALLYLIC CHLORIDES WITH ETHOXIDE ION IN ETHANOL

Chloride	Temp., °C.	k_2[a]	Ratio	Ref.
Allyl	35	0.246	3.7	10
γ-Methylallyl	35	.912		10
γ-Methylallyl	25	.161	5.4	3
γ-Methyl-γ-ethylallyl	25	.870		

[a] Since small amounts of water accelerate the reaction of allylic halides[3] the concentration of each reactant and water are identical for either pair for which comparison is made; k_2 in hr.$^{-1}$ mole^{-1} l.

The kinetics of the reaction of γ-methyl-γ-ethyl allyl chloride with sodium ethoxide in absolute ethanol were essentially second order and the ether isolated from the reaction was at least 98% γ-methyl-γ-ethylallyl ethyl ether.

The second order rate constants were calculated by means of the equation

$$K_2 = \frac{2.30}{t(a - b)} \log \frac{b(a - x)}{a(b - x)}$$

where a is the initial concentration of γ-methyl-γ-ethylallyl chloride (0.905 mole per liter), b is the initial concentration of ethoxide ion (1.07 moles per liter) and x is the concentration of hexenyl chloride reacted in time t. Table II, column 3 shows that the data fit the second order expression with little drift in the rate constant to 51% reaction of chloride. Column 4 contains the rate constants corrected for the small amount of first order reaction which occurs. The corrected values were calculated from the equation.[12]

$$k_2 = K_2 - \frac{k_1}{(b - x)} + t\frac{dK_2}{dt}$$

The data given in Table III were used for these calculations. The effect of ionic strength on the first order reaction was not studied due to interruption of this work by the war. However, unless salt effects prove much greater than anticipated, they are of little concern due to the minor contribution of the solvolytic reaction.

Sufficient data are not yet available for a quantitative demonstration of the relative rates of S_N1 reactions of the gamma substituted allylic halides since it is difficult to accurately evaluate the S_N2 or higher order contributions by the solvent to the first order rate of solvolysis. That substitution in the gamma position does increase the S_N1 rate is qualitatively shown by the fact that the first order rate constant for γ-methyl-γ-ethylallyl chloride ($k_1 = 1.94 \times 10^2$ hr.$^{-1}$; Table III) is nearly one hundred times larger than that for crotyl chloride ($k_1 = 1.84 \times 10^{-4}$ hr.$^{-1}$).[3] The reaction of the disubstituted chloride involves a much larger contribution of S_N1 than that of crotyl chloride as is shown by isolation of the products

TABLE II

KINETICS OF REACTION OF γ-METHYL-γ-ETHYLALLYL CHLORIDE AT 0.905 MOLE PER LITER WITH SODIUM ETHOXIDE AT 1.07 MOLES PER LITER IN ABSOLUTE ETHANOL AT 25.0°

Time, t., min.	NaOEt N	K_2 min.$^{-1}$ mole^{-1}-l.	k_2 cor.
0.0	1.07	0.0148	0.0144
11.5	0.93	.0143	.0139
18.5	.86	.0151	.0147
27.5	.78	.0151	.0147
33.0	.75	.0147	.0142
44.5	.68	.0145	.0140
63.5	.60	.0144	.0136
144	.41[a]	Av. .0147 ± 0.0004	Av. .0142 ± 0.0003
0	1.07	0.0155	0.0151
11.7	0.92	.0150	.0146
18.8	.85	.0160	.0156
32.5	.74	.0154	.0150
38.5	.71	.0154	.0149
46.0	.67	.0151	.0146
52.0	.64	.0148	.0143
58.0	.61[b]	Av.[c] .0153 ± 0.0008	Av. .0148 ± 0.0003

[a] 51% of halide reacted. [b] 36% of halide reacted. [c] When the units of time are changed to hours, k_2 = 0.870 ± 0.02 hr.$^{-1}$ mole^{-1}-l. (mean for two runs).

TABLE III

KINETICS OF THE ALCOHOLYSIS OF THE HEXENYL CHLORIDES IN ABSOLUTE ETHANOL AT 25°

Time, hours	Alkali, ml.	Reacted, %	$k_1$hr.$^{-1}$
α-Methyl-α-ethylallyl chloride 0.554 mole per liter			
3.17	1.51	10.7	0.0336
3.92	1.85	13.1	.0357
4.45	2.09	14.7	.0359
5.08	2.35	16.6	.0358
5.63	2.58	18.2	.0360
6.25	2.83	19.9	.0360
6.92	3.10	21.9	.0359
7.50	3.31	23.4	.0356
8.08	3.52	24.8	.0356
8.50	3.68	26.0	.0356
9.82	4.22	29.8	.0360
		Average	.0358 ± 0.001
γ-Methyl-γ-ethylallyl chloride 0.572 mole per liter			
3.62	1.05	7.2	0.0202
4.92	1.37	9.3	.0198
5.67	1.56	10.7	.0198
6.33	1.71	11.7	.0198
6.93	1.86	12.7	.0196
7.50	1.97	13.4	.0192
8.00	2.09	14.7	.0194
9.33	2.40	16.4	.0193
9.83	2.52	17.3	.0192
10.33	2.62	18.6	.0191
11.00	2.76	18.9	.0190
		Average	.0194 ± 0.001

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

(11) Juvala, *Ber.*, **63**, 1990 (1930).

(12) Hughes, Ingold and Shapiro, *J. Chem. Soc.*, 231 (1938).

of the reaction. Very little rearrangement was observed during the ethanolysis of crotyl chloride[7] whereas the ethanolysis of the disubstituted chloride gives about equal quantities of the tertiary and primary ethyl ethers. Thus the S_N1 rate must have been increased more than the S_N2 rate by substitution, as expected, provided no S_N2′ reaction was taking place. Since the S_N2′ reaction was not observed under more favorable conditions it would hardly be expected here.

Experimental Part

Hexenyl Chlorides.—These two isomeric chlorides were prepared by treating α-methyl-α-ethylallyl alcohol with thionyl chloride and pyridine, phosphorus trichloride and pyridine, acetyl chloride or hydrogen chloride. The best yields (78–83%) were obtained with the highest proportion of α-methyl-α-ethylallyl chloride (35–65%) using hydrogen chloride at 0 to −50°.

α-Methyl-α-ethylallyl alcohol was prepared by hydrogenating α-methyl-α-ethylpropargyl alcohol[13] over a catalyst of palladium deposited on barium sulfate until exactly one mole of hydrogen had been absorbed, b.p. 117–118°, $n^{20}\mathrm{D}$ 1.4288.[13b] Ozonolysis gave formic acid (70%) and α-hydroxy-α-methylbutyric acid (2%), m.p. 70–73°.

α-Methyl-α-ethylallyl Chloride.—B.p. 37.5–39.5° at 60 mm., $n^{25}\mathrm{D}$ 1.4289, $n^{15}\mathrm{D}$ 1.4339. *Anal.* sapon. equiv.: calcd. 118.6, found 122, 125, 126 g. This substance was used shortly after purification but could be stored at 0–5° for several days without change in refractive index when free of water and hydrogen chloride. γ-Methyl-γ-ethylallyl chloride, b.p. 62–63° at 60 mm., $n^{25}\mathrm{D}$ 1.4518, $n^{15}\mathrm{D}$ 1.4567. *Anal.* sapon equiv.: calcd. 118.6, found 119, 120 g. Ozonolysis gave chloroacetaldehyde as the 2,4-dinitrophenylhydrazone.

Kinetics of the Conversion of γ-Methyl-γ-ethylallyl Chloride to Ethyl Ether with Sodium Ethoxide in Absolute Ethanol.—The absolute ethanol used in experiments described in this paper was prepared by drying commercial absolute ethanol (99.7%) with magnesium ethoxide.[14] It contained not more than 0.05% water by the Crismer method.[15]

About 6 g. of clean sodium was dissolved in 210 ml. of absolute ethanol, and the clear colorless solution, after being allowed to stand 2 days, was standardized with 0.2046 *N* H_2SO_4; concentration 1.21 *M*. Alcoholic hydrogen chloride was prepared by passing hydrogen chloride into absolute ethanol. It was standardized with the sodium ethoxide solution, concentration 0.310 *N*. To a 2.00-ml. sample of γ-methyl-γ-ethylallyl chloride, weighing 1.83 g. (0.0154 mole), at 25.0 ± 0.1°, was added 15.00 ml. of sodium ethoxide solution kept at 25.0°. The volumes were assumed to be additive. Aliquots of 2.00 ml. each were withdrawn from time to time and titrated as quickly as possible with the freshly standardized alcoholic hydrogen chloride using phenolphthalein as indicator. The time was recorded at half-titration. Results are shown in Table II.

Isolation of Product from Reaction of γ-Methyl-γ-ethylallyl Chloride with Sodium Ethoxide in Ethanol.—Twenty-three grams of γ-methyl-γ-ethylallyl chloride (0.19 mole) was added at 25° to a solution of sodium ethoxide in absolute ethanol, freshly prepared from 6.5 g. of clean sodium (0.28 mole) and 250 ml. of absolute ethanol. The initial concentrations were about 0.7 *M* chloride and 1 *M* ethoxide. The flask was stoppered and let stand. The solution became cloudy in a few minutes. After a week the mixture was poured into water and extracted with low-boiling petroleum ether. The extract contained no halogen. Fractionation at atmospheric pressure with a 40-in. modified Podbielniak column gave γ-methyl-γ-ethylallyl ethyl ether, b.p. 143–144°, but the refractive indices of successive fractions rose from $n^{25}\mathrm{D}$ 1.4200 to 1.4232. Refractionation very slowly *in vacuo* gave, after a very small forerun, material boiling at 63° at 39 mm., $n^{25}\mathrm{D}$ 1.4233. There may possibly have been as much as 2% yield of α-methyl-α-ethylallyl ethyl ether in the forerun. The yield was 22 g. (89%).

Kinetics of the Alcoholysis of the Hexenyl Chlorides.—Two ml. of hexenyl chloride was weighed accurately to 1 mg. and diluted with 25.00 ml. of absolute ethanol in a glass stoppered bottle at 25°. The solution was maintained in a thermostat at 25.1 ± 0.1°. At frequent intervals, a 2.00-ml. aliquot was removed and titrated immediately with 0.0782 *N* alkali in 95% ethanol using phenolphthalein as indicator. The first order rate constants were calculated from the developed first order rate expression.

$$k_1 = \left(\frac{2.30}{t}\right)\left(\log \frac{100\%}{100\% - \%\ \text{reacted}}\right)\text{hr.}^{-1}$$

The progress of solvolyses is shown in Table III.

Isolation of Ethyl Ethers from Alcoholysis of γ-Methyl-γ-ethylallyl Chloride at 0.56 *M* in Absolute Ethanol.—Thirty-five grams of γ-methyl-γ-ethylallyl chloride (0.30 mole), 30 g. of C.P. calcium carbonate (0.30 mole) and 500 ml. of absolute ethanol were stirred together at room temperature for one week and then refluxed one hour. After decantation from the solid, the solution was diluted with 400 ml. of water and extracted with petroleum ether (b.p. 30–37°) and dried. Analysis with the 40-in. column gave the following two distinct fractions: α-methyl-α-ethylallyl ethyl ether, b.p. 122–124°, $n^{20}\mathrm{D}$ 1.4130, 17.0 g. (50.5%): *Anal.* Calcd. for $C_8H_{16}O$: C, 74.94; H, 12.58. Found: C, 74.85; H, 12.58; γ-methyl-γ-ethylallyl ethyl ether, b.p. 145–147°, $n^{22}\mathrm{D}$ 1.4251, 16.6 g. (49.5%).

Anal. Calcd. for $C_8H_{16}O$: C, 74.94; H, 12.58. Found: C, 74.66; H, 12.85. The yield of ethers was 33.6 g. (89%).

Summary

The reaction of γ-methyl-γ-ethylallyl chloride with sodium ethoxide in ethanol is shown to be bimolecular without allylic rearrangement. The second order rate constant is compared with those of crotyl and allyl chlorides, and thereby it is demonstrated that electron accession at the α-carbon of the allylic system promotes rather than suppresses bimolecular nucleophilic substitution, S_N2. The first order solvolysis constants for α-methyl-α-ethylallyl chloride and γ-methyl-γ-ethylallyl chloride have been measured in ethanol at 25°.

LOS ANGELES 24, CALIFORNIA RECEIVED JULY 17, 1950

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(13) (a) Campbell, Campbell and Eby, THIS JOURNAL, **60**, 2882 (1938); (b) Young and Webb, *ibid.*, **73**, 780 (1951).

(14) Fieser, "Experiments in Organic Chemistry," Part II, D. C. Heath and Co., New York, N. Y., 1941, p. 359.

(15) Robertson, "Laboratory Practices of Organic Chemistry," The Macmillan Co., New York, N. Y., 1937, p. 161.