[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORIES, BROWN UNIVERSITY, PROVIDENCE, R. I.]

# Elimination Reactions of Benzyldimethylcarbinyl Chloride. E2 Reactions Leaning toward E1[1]

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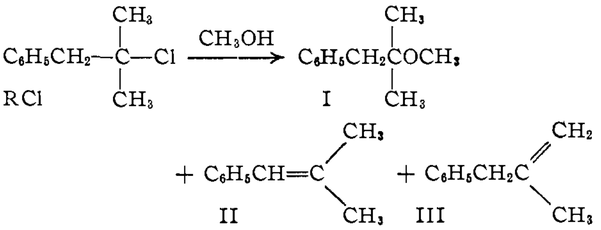
For both benzyldimethylcarbinyl chloride and a dideuterium derivative (deuteriums *alpha* to the benzene ring), kinetics and products of methanolysis and of reactions with $CH_3O^-$ and with $C_2H_5S^-$ in methanol have been determined. The results indicate solvolysis to be unimolecular (E1–SN1) and reactions with the anionic bases to be E2 eliminations. However, remarkably low β-deuterium isotope and β-phenyl substituent effects in the E2 reactions call for a transition state leaning toward the E1 mechanism, in which C–Cl rupture has proceeded much further than C—H breaking, and C=C formation has made little progress. This is a further demonstration that E2 reactions, though concerted, need not be fully synchronous. As a base, thioethoxide ion is ***kinetically*** about ten times stronger than methoxide ion in these reactions.

We have made an intensive study of some elimination reactions of benzyldimethylcarbinyl chloride (RCl) in methanol medium, both in the absence and the presence of basic reagents. The results indicate an unusual type of E2 mechanism for the base-induced eliminations.

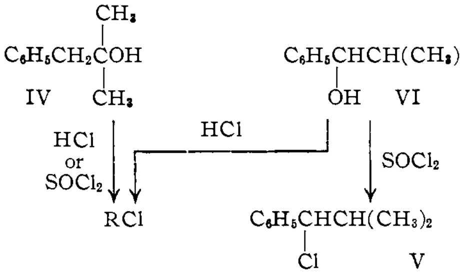
The only previous kinetic work with this substrate is that of Landis and VanderWerf,[3] who determined rates of solvolysis, in 80% aqueous ethanol, of RCl and several of its *p*-substituted derivatives. They did not study the products. The rate of solvolysis of the isomeric chloride phenylisopropylcarbinyl chloride (V) in the same solvent has also been measured.[4]



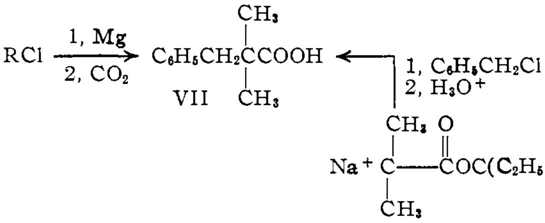
The solvolysis and other reactions which we studied gave three products, one of substitution (ether I) and two of elimination (olefins II and III). β,β-Dimethylstyrene (II) has conjugated unsaturation not present in RCl or the other two products, and consequently is easily determined by photometric measurements in the ultraviolet. This enables rates to be determined with facility. Also, the yield of dimethylstyrene in any run is easily reckoned from the infinity absorbance.

## Descriptive Studies

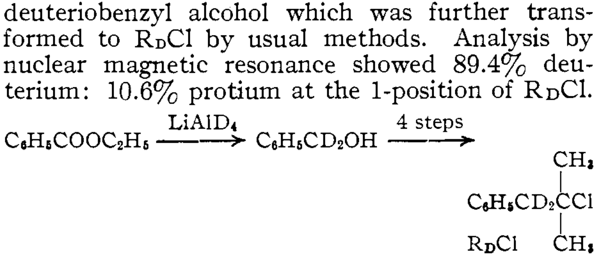
We originally prepared RCl by an adaptation of the method of Landis and VanderWerf.[3] The conditions (treatment of carbinol IV in concentrated hydrochloric acid with hydrogen chloride gas) are conducive to carbonium ion formation, and rearrangement to phenylisopropylcarbinyl chloride (V) was conceivable. Uneasiness was increased by discovery that the isomeric carbinol VI gave the *same chloride* when submitted to the same treatment.



That RCl is truly benzyldimethylcarbinyl chloride was confirmed in two ways. First, carbonation of the Grignard reagent derived from it gave acid VII, identical to an authentic sample prepared by benzylation of the sodium derivative of triethylcarbinyl isobutyrate[5] and subsequent hydrolysis. Second, when carbinols IV and VI were submitted to the action of thionyl chloride, *different* chlorides were formed. These were, respectively, the same RCl as obtained originally and a second chloride presumed to be V. Thus it is shown that rearrangement from the phenylisopropylcarbinyl to the benzyldimethylcarbinyl system occurs on treatment of VI with hydrochloric acid.[6]



1,1-Dideuterio-1-phenyl-2-methyl-2-propyl chloride ($R_DCl$), which is RCl substituted with deuterium in both positions *alpha* to the benzene ring, was also prepared. Reduction of ethyl benzoate with lithium aluminum deuteride gave α,α-dideuteriobenzyl alcohol which was further transformed to $R_DCl$ by usual methods. Analysis by nuclear magnetic resonance showed 89.4% deuterium: 10.6% protium at the 1-position of $R_DCl$.



$$C_6H_5COOC_2H_5 \xrightarrow{LiAlD_4} C_6H_5CD_2OH \xrightarrow{\text{4 steps}} C_6H_5CD_2C(CH_3)_2Cl$$

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[1] Based in part on the Ph.D. Thesis of G. T. Davis, 1959.

[2] On leave from the Shionogi & Co. Research Laboratories, Osaka, Japan, 1959–1960.

[3] A. Landis and C. A. VanderWerf, *J. Am. Chem. Soc.*, **80**, 5277 (1958).

[4] G. Baddeley, J. Chadwick and H. T. Taylor, *J. Chem. Soc.*, 2405 (1954).

[5] C. R. Hauser and W. J. Chambers, *J. Am. Chem. Soc.*, **78**, 3837 (1956).

[6] This transformation has been observed independently by Dr. M. S. Silver, Amherst College.

Pure samples of olefins II and III were prepared by familiar methods and were used in standardizing product analyses by ultraviolet spectrophotometry and vapor phase chromatography (v.p.c.).

## Experimental

**Benzyldimethylcarbinol** (IV), b.p. 99.5–102° (12–14 mm.), $n^{27}_{\mathrm{D}}$ 1.5114 (lit.[3] b.p. 92.5–93° (10 mm.), $n^{30}_{\mathrm{D}}$ 1.5105), was prepared in 74% yield by the Grignard procedure of Landis and VanderWerf.[3]

**Phenylisopropylcarbinol** (VI), b.p. 96–99° (10 mm.) (lit.[7] b.p. 101–104° (7 mm.)), was prepared in 73% yield by the Grignard procedure of Conant and Blatt[7] except that isopropyl iodide was used.

**Treatment of IV with Hydrochloric Acid.**—To 5 g. of anhydrous calcium chloride, 64 g. of IV was added and then 250 cc. of concentrated hydrochloric acid (with cooling). The mixture was agitated frequently during a period of 30 minutes; vivid colors (principally violet) were noticed. The organic layer was separated, washed in a chilled separatory funnel with cold, concentrated sulfuric acid, treated with solid calcium carbonate, taken up in ether and dried over anhydrous sodium sulfate and calcium chloride. After removal of the ether, the residue was distilled; b.p. 86–87° (9–10 mm.), $n^{26}_{\mathrm{D}}$ 1.5120 (reported[3] for benzyldimethylcarbinyl chloride (RCl): b.p. 87–88.5° (10 mm.), $n^{30}_{\mathrm{D}}$ 1.5109). The yield was 33 g. (46%) of colorless liquid.

**Treatment of VI with hydrochloric acid** according to the same procedure gave a product identical in all respects (including infrared spectra) with the above product.

**Benzyldimethylcarbinyl Chloride (RCl) by Thionyl Chloride Method.**—To 150 cc. of thionyl chloride in 1500 cc. of dry toluene at −5 to −10°, 197 g. of IV was added with stirring during a period of 3 hours. The solution was aspirated briefly to remove hydrogen chloride, allowed to stand overnight at room temperature, and distilled at atmospheric pressure (sulfur dioxide was evolved) to remove toluene. The residue was distilled at reduced pressure; 105 g. (48%) of colorless RCl was obtained. Properties, including infrared spectrum, were the same as for the above preparations. (A modified procedure (see $\mathrm{R_DCl}$ below) gave better yields.)

**Phenylisopropylcarbinyl Chloride (V).**—From 14 cc. of thionyl chloride and 25.8 g. of VI in 200 cc. of toluene, by the above procedure, 17.8 g. (62%) of V was obtained; b.p. 88–89° (10 mm.) or 97–97.5° (14–15 mm.), $n^{27}_{\mathrm{D}}$ 1.5129 (lit.[4] b.p. 63–64° (0.5 mm.)). The infrared spectrum differed significantly from spectra of the above preparations of RCl.

*Anal.* Calcd. for $C_{10}H_{13}Cl$: C, 71.19; H, 7.76. Found[8]: C, 71.36, 71.48; H, 7.71, 7.89.

**Phenylpivalic Acid (VII). A. From RCl.**—To 2.4 g. of fine magnesium turnings in 50 cc. of dry ether, 3 drops of ethyl bromide and then 18 g. of RCl in 100 cc. of ether were added according to the usual technique. The resulting Grignard solution was poured onto about 200 g. of solid carbon dioxide covered by 200 cc. of dry ether in a large beaker. After the mixture had warmed to about 0°, 100 cc. of 25% sulfuric acid was added and the ether layer was separated. The aqueous layer was thrice extracted with 50-cc. portions of ether. All the ether layers were combined and extracted with three portions of 25% sodium hydroxide. The basic layer was warmed to expel ether and acidified with sulfuric acid. The white oil which appeared soon solidified. The dried solid (7.0 g., 25%) had m.p. 55–56°, raised to 56–56.5° by crystallization from petroleum ether. Haller and Bauer[9] reported m.p. 57°.

**B. By Independent Synthesis.**—Triethylcarbinyl isobutyrate, b.p. 69–74° (10 mm.) (lit.[5] 68–70° (9.1 mm.), was prepared in 48% yield by the method of Hauser and Chambers.[5] By their procedure, except that sodium amide was used instead of potassium amide, 23.3 g. of this ester was alkylated with 16.2 g. of benzyl chloride. The resulting triethylcarbinyl phenylpivalate (15.1 g., 44%) had b.p. 161–165° (15 mm.). It was hydrolyzed by heating at reflux with 15 cc. of concentrated hydrochloric acid and 10 cc. of dioxane for 2 hours; the product was isolated much as described above. The VII so obtained (8.09 g., 83%) was identical in m.p. and infrared spectrum with the above preparation, and the mixture m.p. was undepressed.

**β,β-Dimethylstyrene (II).**—Isobutyrophenone was converted to phenylisopropylcarbinylamine in 53% yield essentially by the procedure (for α-aminododecylbenzene) of Moore.[10] The product had b.p. 94.5–95° (16 mm.), $n^{27}_{\mathrm{D}}$ 1.5106 (lit.[11] b.p. 95° (14 mm.), $n^{20}_{\mathrm{D}}$ 1.5123). This primary amine was converted to the tertiary amine, phenylisopropylcarbinyldimethylamine, in 57% yield by the Eschweiler–Clarke methylation procedure of Moore.[10] The tertiary amine had b.p. 97–97.5° (15 mm.), $n^{26}_{\mathrm{D}}$ 1.4999 (lit.[12] b.p. 80.5° (1 mm.), $n^{25}_{\mathrm{D}}$ 1.4996). The tertiary amine was oxidized to the N-oxide and thence pyrolyzed to β,β-dimethylstyrene substantially according to the method of Cope, Foster and Towle.[13] The olefin had b.p. 72° (15 mm.), $n^{25}_{\mathrm{D}}$ 1.5367, $\epsilon$ at 244 mμ ($\lambda_{\max}$) 14,470 in methanol (lit.[14] $n^{25}_{\mathrm{D}}$ 1.5364, $\epsilon$ at 244 mμ 14,000 in isoöctane, b.p. 75–79° (12–14 mm.)[15]), and was pure by v.p.c.

**3-Phenyl-2-methylpropene (III).**—The general method of Cornforth, Cornforth and Mathew[16] was used. Reaction of benzylmagnesium chloride (from 42.2 g. of benzyl chloride) with chloroacetone according to the "General Procedure" of these authors produced 33 g. of 1-chloro-2-methyl-3-phenyl-2-propanol, b.p. 100–126° (5–6 mm.) (lit.[17] 160° (40 mm.)), whose infrared spectrum indicated a carbonyl impurity. Treatment of this chlorohydrin with 10.2 g. of potassium hydroxide in 180 cc. of water, with stirring for 70 minutes, with product isolation by usual procedures, furnished 14 g. of 1,2-epoxy-2-methyl-3-phenylpropane, b.p. 97–100° (18 mm.), whose infrared spectrum indicated a carbonyl impurity. A small portion (0.5 g.) was purified by passing it, in benzene solution, through a column of basic alumina which had been pretreated with 2,4-dinitrophenylhydrazine, and final distillation in a Hickman still; the epoxide so obtained boiled at 85–93° (12 mm.) and was carbonyl-free by infrared. *Anal.* Calcd. for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found[8]: C, 81.34; H, 8.09.

Reduction of the main batch of the epoxide to III was performed according to the "One-stage preparation of olefins from epoxides" of Cornforth, *et al.*[16] The III so obtained (2.32 g.), b.p. 61° (19 mm.), $n^{25}_{\mathrm{D}}$ 1.5049, $d^{25}_4$ 0.887, $M_{\mathrm{D}}$ 44.2 (calcd. 44.2), was pure by v.p.c.; lit. values are b.p. 69–70° (20 mm.),[18] $n^{25}_{\mathrm{D}}$ 1.5057.[14] *Anal.* Calcd. for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 90.66; H, 9.18.

**Isolation of Benzyldimethylcarbinyl Methyl Ether (I).**—The product mixture from boiling 26 g. of RCl with 18 g. of sodium bicarbonate in 200 cc. of absolute methanol for 48 hours (under reflux) was isolated by standard methods and fractionated through a good column, and the higher-boiling ether fraction was refractionated. The ether I had b.p. 85.5° (10 mm.), $n^{25}_{\mathrm{D}}$ 1.4948, and was pure by v.p.c. *Anal.* Calcd. for $C_{11}H_{16}O$: C, 80.45; H, 9.82. Found[8]: C, 80.21; H, 9.71.

**α,α-Dideuteriobenzyl Alcohol.**—To a suspension of 5.92 g. (0.129 mole) of lithium aluminum deuteride (Metal Hydrides, Inc.) in 250 cc. of calcium hydride-dried ether under a nitrogen atmosphere was added a solution of 30.8 g. (0.205 mole) of ethyl benzoate in 70 cc. of ether at such a rate as to maintain gentle reflux, during 1.5 hours. After an additional 1.5 hours of reflux, the mixture was treated cautiously with wet ether and then with water. It was poured into 200 cc. of chilled water and 400 cc. of 10% sulfuric acid was added. The layers were separated and the aqueous layer extracted twice with 150-cc. portions of ether. The com-

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(7) J. B. Conant and A. H. Blatt, *J. Am. Chem. Soc.*, **50**, 554 (1928).

(8) Analysis by Micro-Tech Laboratories, Skokie, Ill.

(9) A. Haller and E. Bauer, *Compt. rend.*, **149**, 1 (1909).

(10) M. L. Moore, "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 322.

(11) M. Konowalow, *Ber.*, **28**, 1859 (1895).

(12) A. T. Stewart, Jr., and C. R. Hauser, *J. Am. Chem. Soc.*, **77**, 1098 (1955).

(13) A. C. Cope, T. T. Foster and P. H. Towle, *ibid.*, **71**, 3929 (1949).

(14) S. J. Lapporte, quoted by R. Heck and S. Winstein, *ibid.*, **79**, 3432 (1957).

(15) D. A. Shearer and G. F. Wright, *Can. J. Chem.*, **33**, 1022 (1955).

(16) J. W. Cornforth, R. H. Cornforth and K. K. Mathew, *J. Chem. Soc.*, 112 (1959).

(17) E. Fourneau, *J. Pharm. Chim.*, [7] **2**, 56 (1909); *Chem. Zentr.*, **81**, II, 1366 (1910).

(18) F. D. Whitmore, C. A. Weisgerber and A. C. Shabica, Jr., *J. Am. Chem. Soc.*, **65**, 1468 (1943).

bined ether layers were dried, evaporated and distilled; 19.7 g. (87%) of α,α-dideuteriobenzyl alcohol, b.p. 86–86.5° (9 mm.), was obtained.

**α,α-Dideuteriobenzyl Chloride.**—To 19.7 g. of the above alcohol and 13.5 g. of pyridine in 180 cc. of chloroform was added dropwise a solution of 25.0 g. of thionyl chloride in 70 cc. of chloroform during 40 minutes with ice cooling. The solution was gradually heated to boiling and refluxing was continued until sulfur dioxide was no longer evolved (3 hours). The cooled mixture was treated with chilled water and the chloroform solution was washed repeatedly with water and sodium thiosulfate solution, dried over sodium sulfate and distilled. α,α-Dideuteriobenzyl chloride (19.1 g., 83%) was obtained as a colorless liquid, b.p. 61–62° (11 mm.). The infrared spectrum showed this chloride to have little protium at the benzylic position.[19]

**2-Methyl-1-phenyl-2-propanol-1,1-$d_2$.**—From 16 g. of the above chloride, 3.0 g. of magnesium turnings and 8.2 g. of acetone, by a standard Grignard procedure, 15.8 g. (84%) of this tertiary alcohol was obtained, b.p. 85–85.5° (8 mm.), $n^{31}$D 1.5092.

**1,1-Dideuterio-1-phenyl-2-methyl-2-propyl Chloride ($R_D$-Cl).**—To a solution of 13.4 g. of the above tertiary alcohol and 1.5 g. of pyridine in 170 cc. of benzene was added dropwise a solution of 12.6 g. of thionyl chloride in 50 cc. of benzene with ice cooling. After having stood overnight at room temperature, the solution was boiled for 2.5 hours. The cooled mixture was washed with ice-water, dilute sulfuric acid, aqueous sodium bicarbonate and aqueous sodium thiosulfate, dried and distilled; $R_D$Cl (11.2 g., 75%) was obtained as a colorless liquid, b.p. 86–87° (11 mm.), $n^{23}$D 1.5121. The infrared spectrum showed olefinic impurities to be absent, but was not definitive of deuterium content. The nuclear magnetic resonance spectrum[20] revealed the presence of 10.6% protium among the hydrogen atoms *alpha* to the benzene ring, the remaining 89.4% being deuterium.

The source of this protium contamination is not known. However, it is noteworthy that in two other laboratories[21] deuterated compounds prepared *via* reduction of ethyl esters with lithium aluminum deuteride had almost the identical analysis to ours.

**Product Analyses by Vapor Phase Chromatography. A. Procedure Used for the First Analysis in Table IV and All in Table V.**—The concentration of RCl in reaction solutions (volume usually 40 or 50 cc.) was 0.4 *M*. The reaction solution was sealed in an ampoule, allowed to remain in the thermostat long enough for reaction to be complete, cooled, opened and treated with (solid) sodium bicarbonate to neutralize hydrochloric acid. After filtration, the solution was partially concentrated in a fractionating column at atmospheric pressure, 10 to 20 cc. of cyclohexane or *n*-heptane was added, and precipitated salts were filtered off. After further concentration to 15 to 20 cc., a portion of the remaining solution was introduced into a Perkin–Elmer model 154 vapor phase fractometer, with column "C" (silicone fluid), at a temperature of about 135°.

Three peaks, nicely separated, were observed in each product chromatogram. These corresponded exactly in retention times to chromatograms of pure samples of I, II and III. In only one experiment (Table V) was evidence for any other product found, and that apparently an isomeric olefin formed under unusually strenuous conditions.

**B. Procedure Used for Most Analyses in Table IV.**—A smaller scale was employed: 10-cc. reaction solutions 0.1 *M* in RCl or $R_D$Cl. Although known synthetic mixtures of I, II and III gave correct analyses after being run through concentration procedure A, appropriately smaller quantities gave results somewhat low in II and III, suggesting small losses through co-distillation with methanol. The following procedure was therefore used for runs on the smaller scale. The cooled reaction tube was opened and combined with 35 cc. of cyclohexane and 25 cc. of water. After separation of the cyclohexane layer, the water layer was extracted with two 25-cc. portions of cyclohexane. The combined cyclohexane layers were washed by 20 cc. of 0.8% sulfuric acid, 5 cc. of water and 5 cc. of saturated sodium bicarbonate solution, dried over anhydrous sodium sulfate and concentrated to a volume of 1 cc. by distillation in a Widmer column at atmospheric pressure. Portions of this concentrate were introduced into the same vapor phase fractometer as above. Analyses of synthetic mixtures of I, II and III gave results for each component within about 1% of the true content; the relative error is thus within about 3%.

Products of reaction of RCl with $NaOCH_3$ and $NaSC_2H_5$ were also analyzed by a modification of procedure A, and the results (not reported) were in substantial agreement with those in Table IV under corresponding conditions. In reactions with $NaSC_2H_5$, no peak which could be assigned to benzyldimethylcarbinyl ethyl sulfide was ever found, although a small amount of a product (perhaps diethyl disulfide) with a very short retention time was noted. With this exception, I, II and III were the only products found under any conditions.

**Kinetic Measurements.**—Reagent grade methanol was dried with use of magnesium metal. Sodium methoxide solutions were made by dissolving freshly cut sodium in methanol; they were standardized by titration against potassium biphthalate. Sodium thioethoxide solutions were prepared by pipetting known amounts of an ethyl mercaptan standard solution and a sodium methoxide standard solution into an appropriate volume of methanol immediately before use. Sodium perchlorate standard solutions were made by dissolving the carefully dried salt in methanol. Amines and amine hydrochlorides used in some experiments were purified or prepared by standard methods.

All runs were performed in sealed ampoules under dry nitrogen. For solvolysis and sodium methoxide runs, RCl or $R_D$Cl was uniformly 0.001 *M*. Usually twelve 5-cc. aliquots of a reaction solution were used. All the ampoules were placed in the thermostat at once and individual ampoules were removed at recorded times and plunged into ice-cold water. "Infinity" ampoules were removed after at least eight half-lives and usually two were taken for each run. The contents of each ampoule were rinsed into a 25- or 50-cc. volumetric flask and diluted to the mark with methanol. Absorbances were read on a Beckman DU spectrophotometer at 244 mμ, a wave length at which product mixtures routinely showed maximum absorption. Plots of log $(A_\infty - A_t)$ *versus* time, where $A_\infty$ and $A_t$ are absorbances at "infinity" and at any time, were uniformly linear. The slopes multiplied by −2.30 gave the pseudo-first-order rate coefficients.

For thioethoxide runs, reaction solutions were usually 0.01 *M* in RCl or $R_D$Cl. In order to ensure complete conversion to thioethoxide ion, a 50% excess of ethyl mercaptan was usually present; 1-cc. aliquots were sealed in ampoules, etc., as above. When the ampoules were opened, their contents were treated with a small excess of 0.2 *M* acetic acid in methanol and diluted 125- to 425-fold with methanol before photometric observation. Acidification was necessary because the high absorbance of thioethoxide ion would have obscured absorbance due to II; ethyl mercaptan absorbs much less strongly than its anion.[22] Nevertheless, at the highest concentrations of $NaSC_2H_5$, absorption by the mercaptan caused a decrease in the precision of the measurements. Again pseudo-first-order kinetics were observed and rate coefficients were reckoned as described.

Although these measurements are based on determination of only one of three products, the rate coefficients represent the sum of all reactions consuming RCl or $R_D$Cl.[23] This statement involves the assumptions that the three products are formed in constant ratio throughout any run and that they are not interconverted after being formed. The latter assumption was checked in part: solutions of the pure olefins in 1 *M* sodium methoxide suffered no change in absorbance during 11 hours at 75.7°. Also, the "infinity" absorbance in solvolysis runs was shown not to change during an additional 23 half-lives.

Data from a representative run are presented in Table I.

**Confirmatory Kinetic Runs by Titration for Chloride Ion.**[24]—In a sodium methoxide run at 75.8°, $[RCl]_0$ was

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(19) We thank Dr. Wm. T. King for counsel in interpretation of the infrared spectrum.

(20) Taken and interpreted by N. S. Bhacca, Varian Associates, Palo Alto, Calif.

(21) W. H. Saunders, Jr., S. Ašperger and D. H. Edison, *J. Am. Chem. Soc.*, **80**, 2421 (1958); V. J. Shiner, Jr., *ibid.*, **83**, 240 (1961).

(22) H. Ley and B. Arends, *Z. physik. Chem.*, **B15**, 311 (1932).

(23) J. F. Bunnett, E. W. Garbisch, Jr., and K. M. Pruitt, *J. Am. Chem. Soc.*, **79**, 385 (1957); H. T. Liang and P. D. Bartlett, *ibid.*, **80**, 3585 (1958).

(24) We are grateful to Dr. Walter Greizerstein for performing these runs.

0.0500 $M$ and $[NaOCH_3]_0$ 0.566 $M$. Aliquots (5 cc.) were sealed in ampoules, placed in the thermostat, and removed at recorded times as described above. The chilled contents were treated with 5 cc. of 30% nitric acid and immediately extracted with 10 cc. of diethyl ether. Chloride ion was determined potentiometrically in the aqueous layer. The $k_\psi$ value so determined was 2.56 × $10^{-4}$ sec.$^{-1}$. This compares with 2.50 × $10^{-4}$ sec.$^{-1}$ interpolated from data in Table II.

In a sodium thioethoxide run at 75.8°, $[RCl]_0$ was 0.0484 $M$, $[NaSC_2H_5]_0$ 0.566 $M$ and $[C_2H_5SH]_0$ 0.331 $M$. The procedure was the same, except that the chilled contents of each ampoule were treated with 5 cc. of 2 $N$ sulfuric acid, and then quickly extracted in succession with 10 cc. of carbon tetrachloride and 10 cc. of ether. To each aqueous layer, 1 cc. each of concentrated nitric acid and of 30% hydrogen peroxide were added. Titration was performed the following day. The $k_\psi$ value so determined was 9.87 × $10^{-4}$ sec.$^{-1}$. This compares with 9.43 × $10^{-4}$ sec.$^{-1}$ interpolated from data in Table II.

In both check runs, the infinity chloride titer was within 2% of the theoretical.

TABLE I

REACTION OF RCl WITH METHANOL CONTAINING $NaClO_4$; A TYPICAL RUN

Initial concentrations: RCl, 0.0010 $M$; $NaClO_4$, 0.100$M$ (room temperature); RCl, 0.00094 $M$; $NaClO_4$, 0.094 $M$ (at 75.8°); temperature 75.85°. Aliquots (5 cc.) were diluted to 50 cc. for spectrophotometric examination.

| Time, min. | Absorbance at 244 mμ | $A_\infty - A_t$ | $1 + \log (A_\infty - A_t)$ |
|---|---|---|---|
| 5 | 0.047 | 0.379 | 0.579 |
| 12 | .077 | .349 | .543 |
| 20 | .113 | .313 | .496 |
| 30 | .148 | .278 | .444 |
| 40 | .181 | .245 | .389 |
| 50 | .207 | .219 | .340 |
| 65 | .246 | .180 | .255 |
| 80 | .281 | .145 | .161 |
| 100 | .312 | .114 | .057 |
| 120 | .333 | .093 | − .032 |
| ∞ | .425 | | |
| ∞ | .426 | | |

The plot of $\log(A_\infty - A_t)$ *vs.* time was linear with slope −5.44 × $10^{-3}$ min.$^{-1}$; multiplied by −2.30/60, this gave the rate coefficient 2.09 × $10^{-4}$ sec.$^{-1}$. The infinity absorbance indicates 29% of dimethylstyrene in the product mixture.

## Results

**Kinetics.**—The rates of solvolysis of RCl and $R_DCl$ were measured in pure methanol and as affected by varying concentrations of sodium perchlorate and, in one run, lithium chloride.

Rates of reactions of both substrates with varying concentrations of sodium methoxide and sodium thioethoxide in methanol were also measured. The principal results are summarized in Tables II and III, and are presented graphically in Figs. 1 and 2.

The rate coefficients listed in these tables represent total rates of destruction of RCl and $R_DCl$. In the case of the deuterated substrate, a correction was applied to the measured ($k_\psi$) rate coefficients to remove the effect of the 10.6% of protium present at the carbon *alpha* to the ring. Corrections were made with use of the expression: $k_\psi = 0.894k_D + 0.106k_H$, where $k_D$ and $k_H$ are pseudo-first-order coefficients for the compounds fully deuterated and fully protiated, respectively, at the position of interest.[25] $k_H$-values were interpolated from the measurements on RCl. Discussions of the kinetic effect of deuterium should be made in terms of $k_D$ values.

TABLE II

RATES OF DESTRUCTION OF BENZYLDIMETHYLCARBINYL CHLORIDE (RCl) IN $CH_3OH$ AT 75.8 ± 0.1°

| Added substances: Identity | Added substances: Concn., $M$[a] | $k_\psi$,[b] sec.$^{-1}$ × $10^4$ | Yield of II, % |
|---|---|---|---|
| None | . . . | 1.43 | 30 |
| | | 1.47 | 30 |
| | | 1.22 | 33 |
| | | 1.53 | 29 |
| | | 1.31[c] | 32 |
| | | 1.20 | 33 |
| | | 1.49[d] | 29 |
| $NaClO_4$ | 0.094 | 2.09 | 29 |
| | .472 | 3.61 | 32 |
| | .707 | 4.43 | 33 |
| LiCl | .095 | 1.84 | 31 |
| $NaOCH_3$ | .023 | 1.49 | 31 |
| | .044 | 1.61 | 30 |
| | .152 | 1.78 | 40 |
| | .253 | 2.12 | 43 |
| | .356 | 2.18 | 47 |
| | .505 | 2.33 | 52 |
| | .505 | 2.52 | 52 |
| | .660 | 2.62 | 58 |
| | .755 | 2.42[e] | 64 |
| | .755 | 2.83 | 61 |
| | .755 | 2.92 | 57 |
| $NaOCH_3$ | .755 | 3.33 | 58 |
| $H_2O$ | .262 | | |
| $NaOCH_3$ | .494 | 3.78 | 45 |
| $NaClO_4$ | .377 | | |
| $NaSC_2H_5$ | .197 | 4.32 | (54)[f] |
| $C_2H_5SH$ | .086 | | |
| $NaSC_2H_5$ | .395 | 6.90 | (61)[f] |
| $C_2H_5SH$ | .171 | | |
| $NaSC_2H_5$ | .592 | 9.82 | [f] |
| $C_2H_5SH$ | .351 | | |
| $NaSC_2H_5$[c] | .869 | (12.8)[f] | (64)[f] |
| $C_2H_5SH$ | .433 | | |

[a] Corrected for solvent expansion. [b] $k_\psi$ is the pseudo-first-order rate coefficient. [c] $[RCl]_0 = 0.02$ $M$. [d] The mean $k_\psi$ for solvolysis is 1.38 × $10^4$ sec.$^{-1}$. [e] Not used in the least squares computation. [f] Owing to absorption by $C_2H_5SH$, the estimates of yield of II are approximate even at low $[NaSC_2H_5]$; the rate coefficient at 0.92 $M$ $NaSC_2H_5$ is regarded as approximate for the same reason.

For one $NaOCH_3$ run and one $NaSC_2H_5$ run, the progress of the reaction was followed by titration of the chloride ion formed. Agreement with rate coefficients from photometric analysis was good. The validity of the photometric rate data is thus affirmed.

Each of the sodium salts caused a linear acceleration of rate. Acceleration increased in the order: $NaOCH_3 < NaClO_4 < NaSC_2H_5$. The slopes in plots of $k_\psi$ *versus* [NaX] (Figs. 1 and 2) are, re-

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[25] This expression would be strictly correct if the sample were a mixture of RCl and pure $R_DCl$. However, the protiums are probably statistically distributed, the majority being in molecules containing one H and one D at the position of interest. Insofar as removal of hydrogen enters the rate-determining step, as it appears to in reactions with the basic reagents (*vide infra*), such molecule would react more nearly at the rate characteristic of RCl than of $R_DCl$. The strictly correct expression would involve dissection of each reaction into parts in which breaking of the bonds in question did and did not enter into rate determination, consideration of the isotope effect in each part, etc. It would be very complex and, since the additional correction would be small in any case, it seems not worth the trouble.

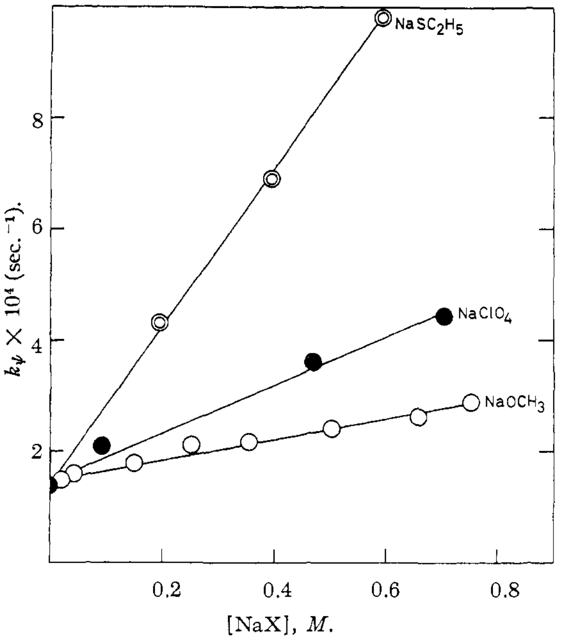

Fig. 1.—Total pseudo-first-order rates of destruction of benzyldimethylcarbinyl chloride (RCl) in $CH_3OH$ as affected by various added substances: ◑, solvolysis; ○, $NaOCH_3$; ●, $NaClO_4$; ◎, $NaSC_2H_5$; data from Table II.

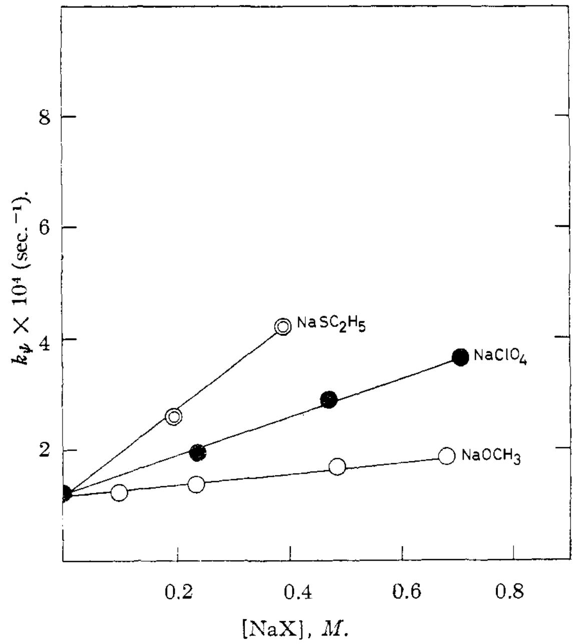

Fig. 2.—Total pseudo-first-order rates of destruction of $R_DCl$ in $CH_3OH$ as affected by various added substances: ◑, solvolysis; ○, $NaOCH_3$; ●, $NaClO_4$; ◎, $NaSC_2H_5$; data from Table III.

spectively, 1.90, 4.35 and 14.2 for RCl, and 1.02, 3.44 and 7.62 for $R_DCl$ (all in units of l. mole$^{-1}$ sec.$^{-1}$ × $10^{-4}$).

**Products.**—The "infinity" absorbances in kinetic runs gave, incidentally, the yields of dimethylstyrene produced. Such photometric yields are listed in Tables II and III.

The products of several reactions were analyzed by vapor phase chromatography. The yields of I, II and III under various conditions are presented in Table IV. Identification of the three peaks on each chromatogram was confirmed by the identity of retention times under standard conditions with those for pure samples of I, II and III.

TABLE III

RATES OF DESTRUCTION OF 1,1-DIDEUTERIO-1-PHENYL-2-METHYL-2-PROPYL CHLORIDE ($R_DCl$) IN $CH_3OH$ AT 75.8 ± 0.1°[a]

| Added substances | | $k\psi$, | Yield of | $k_D$,[c] |
|---|---|---|---|---|
| Identity | Concn., M[b] | sec.$^{-1}$ × $10^4$ | II, % | sec.$^{-1}$ × $10^4$ |
| None | ... | 1.28 | 18 | 1.22 |
| | | 1.18 | 20 | |
| $NaClO_4$ | 0.236 | 2.01 | 20 | 1.93 |
| | .472 | 2.96 | 20 | 2.89 |
| | .707 | 3.72 | 21 | 3.63 |
| $NaOCH_3$ | .097 | 1.28 | 23 | 1.23 |
| | .234 | 1.43 | 27 | 1.37 |
| | .486 | 1.76 | 32 | 1.69 |
| | .681 | 1.96 | 35 | 1.86 |
| $NaSC_2H_5$<br>$C_2H_5SH$ | .194<br>.089 | 2.82 | (45)[d] | 2.59 |
| $NaSC_2H_5$[e]<br>$C_2H_5SH$ | .390<br>.176 | 4.59 | (50)[d] | 4.21 |

[a] The 1-position contains 10.6% protium; see text. [b] Corrected for solvent expansion. [c] $k_D$ is the calculated rate coefficient for the compound completely deuterated at the 1-position. [d] See footnote *f*, Table II. [e] $[R_DCl]_0$ = 0.02 *M*.

The last column in Table IV gives photometric yields of II under the specified conditions, where available. Agreement with the v.p.c. results is excellent.

TABLE IV

PRODUCTS OF DECOMPOSITION OF RCl AND $R_DCl$ IN THE PRESENCE OF DIVERSE SUBSTANCES IN METHANOL SOLUTION AT 75.8°

| Added substances | Substrate[a] | Products, %[b] I | II | III | Photometric yield of II, %[c] |
|---|---|---|---|---|---|
| 2,6-Lutidine, 0.38 *M*<br>2,6-Lutidinium chloride, 0.19 *M* | RCl[d] | 41.2 | 34.3 | 24.5 | |
| Piperidine, 0.19 *M*<br>Piperidinium chloride, 0.09 *M* | RCl | 44.9 | 30.2 | 24.9 | 30.1 |
| | $R_DCl$, exptl. | 52.2 | 19.1 | 28.7 | 18.9 |
| | *$R_DCl$, corr.* | *53.0* | *17.9* | *29.1* | |
| $NaClO_4$, 0.47 *M*<br>Piperidine, 0.19 *M*<br>Piperidinium chloride, 0.09 *M* | RCl | 43.5 | 31.5 | 25.0 | 31.7 |
| | $R_DCl$, exptl. | 48.7 | 21.2 | 30.1 | 20.5 |
| | *$R_DCl$, corr.* | *49.3* | *20.0* | *30.7* | |
| $NaOCH_3$, 1.90 *M*[e] | RCl | 7.6 | 71.5 | 20.9 | |
| | $R_DCl$, exptl. | 11.9 | 50.2 | 37.9 | |
| | *$R_DCl$, corr.* | *12.4* | *47.8* | *39.8* | |
| $NaSC_2H_5$, 0.54 M[e] | RCl | 7.8 | 62.7 | 29.5 | (62)[f] |
| | $R_DCl$, exptl. | 10.6 | 48.2 | 41.2 | (51)[f] |
| | *$R_DCl$, corr.* | *10.9* | *46.6* | *42.5* | |
| $NaSC_2H_5$, 0.92 M[e] | RCl | 3.8 | 65.8 | 30.4 | (64)[f] |
| | $R_DCl$, exptl. | 6.3 | 51.6 | 42.1 | |
| | *$R_DCl$, corr.* | *6.6* | *50.0* | *43.4* | |

[a] "$R_DCl$, exptl." refers to actual measurements on our sample of $R_DCl$; "$R_DCl$, corr." gives yields computed for the compound *fully* deuterated at the 1-position. [b] Analyses by v.p.c. procedure B. [c] From Table II, III or the text. [d] This analysis by v.p.c. procedure A. [e] This is the initial base concentration less half the initial substrate concentration. [f] The precision in these photometric measurements is low.

In Table IV, product analyses from RDCl have been corrected to remove the effect of the 10.6% of protium at the deuterated position. The corrected values, given in italics, were arrived at by increasing the divergence of each value from that for RCl by 1/9.[26]

With the photometric method of analysis, some attention was given to the composition of products from reaction of RCl with mixtures of a constant concentration of sodium methoxide (0.395 *M*) and varying concentrations of sodium perchlorate. The percentages of dimethylstyrene found are shown in Fig. 3. The dashed lines in this figure will be referred to in the Discussion.

**Products of Solvolysis.**—In early experiments for v.p.c. determination of solvolysis products (the first three lines of Table V), the percentages of dimethylstyrene found were much higher than from photometric measurements on kinetic "infinity" solutions. In these experiments, the initial substrate concentration was *ca.* 0.4 *M* whereas it was 0.001 *M* in the kinetic runs. We hypothesized that hydrochloric acid liberated in solvolysis brought about partial or total equilibration among the products with consequent enrichment in the thermodynamically favored olefin. At the low concentration of the kinetic runs, equilibration would (if its rate were proportional to acid concentration) take 400 times as long and would possibly not progress far from the kinetically determined product ratio.

Solvolysis in the presence of enough 2,6-lutidine to neutralize the hydrochloric acid liberated, plus some 2,6-lutidine hydrochloride to repress methoxide formation (by interaction of amine with methanol), gave a product distribution quite different from that in the absence of bases. Compare the first line in Table IV with the first three lines in Table V. The fraction of dimethylstyrene now agreed with that from the kinetics runs (34% *vs.* 31%). 2,6-Lutidine was chosen as a hydrogen chloride acceptor because the steric hindrance about its nitrogen would diminish E2 activity *versus* RCl.[27]

It was discovered that the percentage of dimethylstyrene formed in such experiments was independent of the identity of the amine. This is shown by comparison of the first two lines in Table IV, and by the following yields of II formed by solvolysis in the presence of the amines indicated, with photometric analysis[28]: ammonia, 32.8%; *n*-butylamine, 33.6%; piperidine, 31.7%. The differences between these values and the yields of II at high dilution in pure methanol (Table II) are within experimental error. This concordance indicates that the amines and amine hydrochlorides do not affect product composition,[29] and therefore that products formed in their presence are truly representative of the solvolysis reaction.

Results of some experiments on equilibration of products in the presence of hydrochloric acid are given in Table V. It is clear that equilibration occurs, but also that equilibrium was not uniformly attained, if ever. However, initial slopes in preliminary kinetic runs (not reported) indicated that equilibration of the olefins was relatively fast (half-lives of *ca.* 2 hr. in 0.4 or 0.5 *M* HCl in methanol at 75.7°). The difficulty is that hydrogen chloride reacts with methanol to form methyl chloride[30]; the titer of 0.32 *M* methanolic HCl dropped to 0.04 *M* during 19 hours at 75.7°. When these results were plotted with triangular coördinates,[1] it became clear that all of them tended toward an equilibrium position which is approximately represented by the products of the first four experiments in Table V.

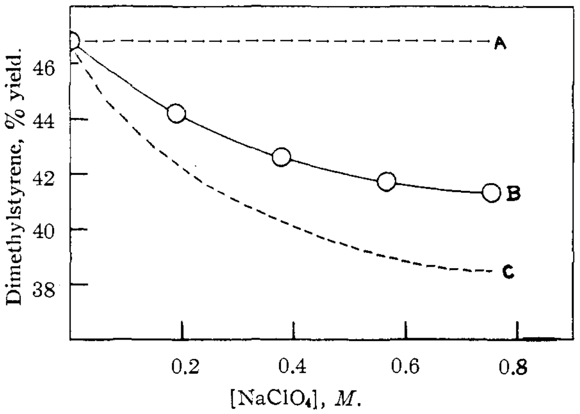

Fig. 3.—Yields of dimethylstyrene (II) formed from RCl in presence of 0.395 *M* NaOCH$_3$ and varying concentrations of NaClO$_4$. The "A" line indicates yields expected on an all E1 hypothesis. The "C" curve indicates yields expected for a mixture of solvolysis, dependent only on [NaClO$_4$], and E2 reaction with NaOCH$_3$. The "B" curve is experimental.

## Discussion

The previous research most nearly analogous to ours is that of Dhar, Hughes and Ingold,[31] who determined rates and products from the reactions of *t*-butyl and *t*-amyl bromides with various concentrations of sodium ethoxide in ethanol. Also directly relevant is de la Mare and Vernon's study[32] which showed sodium thiophenoxide to surpass sodium ethoxide in producing olefin from *t*-butyl chloride. Both groups interpreted their observations in terms of an underlying unimolecular solvolysis (E1 and S$_N$1)[33] plus a superimposed E2 reaction[33] at higher base concentrations.

TABLE V

SOLVOLYSIS OF RCl UNDER EQUILIBRATION CONDITIONS, AND EQUILIBRATION STUDIES ON PRODUCTS (IN METHANOL AT 75.7°)[a]

| | Product composition, % | | |
|---|---|---|---|
| Reactants | I | II | III |
| Solvolysis | 52.2 | 44.4 | 3.5 |
| | 54.3 | 41.7 | 3.9 |
| | 59.3 | 38.1 | 2.5 |
| Solvolysis in 0.51 *M* HCl | 54.0 | 44.1 | 2.0 |
| I in 0.51 *M* HCl | 64.4 | 32.9 | 2.6 |
| II in 0.42 *M* HCl | 25.9 | 70.9 | 3.0 |
| III in 0.39 *M* HCl | 60.3 | 32.6 | 7.3 |
| *Ca.* 80% II:20% III[b] in 0.51 *M* HCl | 42.1 | 55.6 | 2.3 |
| *Ca.* 80% II:20% III[b] in 0.75 *M* HCl[c] | 46.8 | 49.2 | 2.5 |

[a] Reaction time: *ca.* 48 hr.; analysis by v.p.c. procedure A. [b] Olefin mixture obtained by refluxing RCl with 3 *M* NaOH$_3$ in CH$_3$OH. [c] Reaction time: 6 days; an additional substance of retention time similar to II and III constituted 1.4% of the mixture.

We shall discuss our results in the same way, and later consider alternative interpretations.

One can dissect the measured rates and products for the thioethoxide and methoxide reactions into

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(26) While this correction lacks mathematical rigor, it is chemically sufficient. Most of the corrections are on the order of magnitude of the experimental error; further refinement by use of a more sophisticated formula would be of dubious chemical meaning.

(27) J. G. Pritchard and F. A. Long, *J. Am. Chem. Soc.*, **78**, 6008 (1956).

(28) In these experiments, [RCl]$_0$ was 0.001 *M* and the amine and amine hydrochloride 0.19 *M*.

(29) If the amines did enter into product determination, such diverse types would surely not all have the same effect.

(30) C. N. Hinshelwood, *J. Chem. Soc.*, 599 (1935).

(31) M. L. Dhar, E. D. Hughes and C. K. Ingold, *ibid.*, 2065 (1948).

(32) P. B. D. de la Mare and C. A. Vernon, *ibid.*, 41 (1956).

(33) M. L. Dhar, E. D. Hughes, C. K. Ingold, A. M. M. Mandour, G. A. Maw and L. I. Woolf, *ibid.*, 2093 (1948); C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Ch. VIII.

parts derived from solvolysis and from E2 reactions with the bases.[31] One assumes (1) that the rate and (2) the products of solvolysis are unaffected by the presence of the bases, (3) that the bimolecular rate coefficients for reactions with the bases are not dependent on their concentrations, and (4) that no $S_N2$ displacement occurs. From the fraction of ether I formed in the presence of $NaOCH_3$ or $NaSC_2H_5$, the fractions of II and III produced by solvolysis are reckoned with reference to the solvolysis product ratio. These are then subtracted from the total fractions of II and III, leaving the fractions produced by E2 reactions with $NaOCH_3$ or $NaSC_2H_5$. The fraction of the total product stemming from the latter reactions is then easily computed, and is compared with the same quantity as derived from kinetic information. The fractions of II and of III in the olefins from reaction with $NaOCH_3$ or $NaSC_2H_5$ follow directly, and when multiplied by the total second-order rate coefficient (the relevant slope in Fig. 1 or 2) give $k_{II}$ and $k_{III}$, the second-order coefficients for reactions forming the two olefins. Table VI summarizes the outcome of such dissection as applied to all appropriate data. A typical dissection is given as an example.

**Dissection of Products; Representative Example** (*Cf.* Table VI).—For reaction of RCl with 0.92 *M* $NaSC_2H_5$, the product fractions (Table IV) are 0.038 I, 0.658 II and 0.304 III. On the assumptions that I comes entirely from solvolysis and that the solvolysis product ratio is invariant, the fractions from solvolysis are 0.038 I, 0.026 II and 0.021 III; total 0.085. The fractions of total product from reaction with $NaSC_2H_5$ are then 0.632 II and 0.283 III; total 0.915. The fraction of II in the olefins from the latter reaction is 0.632/0.915 = 0.691. The total rate (units of $sec.^{-1} \times 10^{-4}$) is calculated to be 1.38 (solvolysis) plus (0.92)(14.2) (reaction with $NaSC_2H_5$) or 14.45. From kinetics, the fraction of reaction with $NaSC_2H_5$ is then (0.92) (14.2)/(14.45) = 0.905; $k_{II}$ and $k_{III}$, the second-order rate coefficients for elimination to II and to III, are (0.691) (14.2) or 9.85 and (0.309)(14.2) or 4.35, respectively (in $l. mole^{-1} sec.^{-1} \times 10^{-4}$).

The results of this analysis have a high degree of internal consistency. They are best with the sulfur reagent; note the agreement of the fractions of reaction due to reactions with $NaSC_2H_5$ from rates and from products, and the accord between the fractions of II in the olefins from reaction with $NaSC_2H_5$ at two sodium thioethoxide concentrations, for both RCl and $R_DCl$. For sodium methoxide reactions, the products indicate somewhat more reaction with $NaOCH_3$ than do the rates.[34]

TABLE VI

DISSECTION OF RATES AND PRODUCT YIELDS, REACTIONS OF RCl AND $R_DCl$ WITH $NaOCH_3$ AND $NaSC_2H_5$[a]

| Sub-strate | NaX, *M* | E2 Fraction of total reaction From rates | From products | Fraction of II in olefins from E2 | $k_{II}$[b] | $k_{III}$[b] |
|---|---|---|---|---|---|---|
| RCl | $NaOCH_3$, 1.90 | 0.723 | 0.831 | 0.800 | 1.52 | 0.38 |
| $R_DCl$ | $NaOCH_3$, 1.90 | .614 | .766 | .569 | 0.58 | .44 |
| RCl | $NaSC_2H_5$, 0.54 | .846 | .827 | .695 | 9.85 | 4.35 |
| | 0.92 | .905 | .915 | .691 | | |
| $R_DCl$ | $NaSC_2H_5$, 0.54 | .771 | .794 | .541 | 4.14 | 3.50 |
| | 0.92 | .852 | .876 | .545 | | |

[a] Computed from data in Tables II, III and IV, on assumption of mixed solvolysis and E2 with NaX. [b] Units of $l. mole^{-1} sec.^{-1} \times 10^{-4}$.

Two kinetic features of the E2 reactions are noteworthy. First, the accelerating effect of the $\beta$-phenyl substituent is surprisingly small. The ratio $3k_{II}/k_{III}$ represents the enhancement of rate caused by the introduction of a $\beta$-phenyl group. The factor of 3 is needed to compensate for the differing numbers of $\beta$-hydrogens in the methyl *vs.* benzyl branches.[36] Values of $3k_{II}/k_{III}$ are 12 for the methoxide and 6.8 for the thioethoxide reaction. In contrast, introduction of a $\beta$-phenyl group into ethyl bromide effects a 524-fold increase in rate.[37]

Second, the deuterium isotope effect on E2 into the benzyl branch of RCl is unexpectedly low. The ratio $k_{II}(RCl)/k_{II}(R_DCl)$ is only 2.6 (with $NaOCH_3$) or 2.4 (with $NaSC_2H_5$). These contrast with the 6.0-fold deceleration of E2 from $\beta$-phenylethyl bromide (with $C_2H_5O^-$ at 50°) caused by introduction of $\beta$-deuterium atoms.[38] Deuterium isotope effects on the order of six to eight have been the rule in bimolecular elimination from alkyl halides.[38,39] Only a small part of the difference can be assigned to the difference in temperature between our experiments (75.7°) and the others cited (mostly 30–50°).

These points of difference from "typical" E2 reactions indicate an unusual transition state. In recent years it has been recognized that E2 reactions, though concerted, need not be fully synchronous.[40] Though the $C_\alpha$–X and $C_\beta$-H bonds are both ruptured in the same single step,

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(34) The discrepancy presumably stems from imperfection in one or both of assumptions 1 and 2 underlying the dissection. Certain unimolecular solvolyses in aqueous dioxane or methanol are slightly *retarded* by sodium hydroxide or sodium methoxide, respectively.[35] Such an effect in the present system would operate in the direction of the discrepancy noted. As for assumption 2, we know of no definite data concerning the fate of carbonium ions produced in the presence of bases. Nor is the assumption that reaction with the solvent would predominate required by the theory of E1 reactions.[32] Indeed, it is expected that basic reagents would compete with the solvent, forming products (of substitution and/or elimination) in proportions unique for each base. Such competition, insofar as elimination is concerned, should be strongest from the lyate ion because of its special ubiquitous nature.[35c] Insofar as such products were richer in olefins, the fraction of bimolecular reaction with $NaOCH_3$ in Table VI would be overestimated.

(35) (a) G. R. Lucas and L. P. Hammett, *J. Am. Chem. Soc.*, **64**, 1929 (1942); (b) E. F. J. Duynstee, E. Grunwald and M. L. Kaplan, *ibid.*, **82**, 5654 (1960); (c) O. T. Benfey, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 2494 (1952).

(36) This interpretation of $3k_{II}/k_{III}$ is valid if introduction of a phenyl group into one methyl branch of *t*-butyl chloride does not change the E2 rate into the other branches. To the extent that carbonium character at $C_\alpha$ favors faster elimination, a $\beta$-phenyl group should repress elimination into the other branches. Therefore $3k_{II}/k_{III}$ may be an over-estimate of the acceleration due to the $\beta$-phenyl group.

(37) Data of M. L. Dhar, E. D. Hughes, C. K. Ingold and S. Masterman, *J. Chem. Soc.*, 2055 (1948), statistically adjusted for the number of $\beta$-hydrogens available.

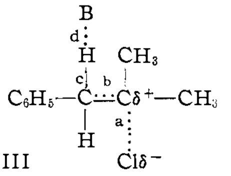
(38) W. H. Saunders, Jr., and D. H. Edison, *J. Am. Chem. Soc.*, **82**, 138 (1960).

(39) V. J. Shiner, Jr., *ibid.*, **74**, 5285 (1952); V. J. Shiner, Jr., and M. L. Smith, *ibid.*, **80**, 4095 (1958).

(40) (a) D. J. Cram, F. D. Greene and C. H. DePuy, *ibid.*, **78**, 790 (1956); (b) J. Weinstock, R. G. Pearson and F. G. Bordwell, *ibid.*, **78**, 3473 (1956); (c) C. H. DePuy and C. A. Bishop, *ibid.*, **82**, 2532 (1960); (d) E. D. Hughes and J. C. Maynard, *J. Chem. Soc.*, 4087 (1960); (e) D. V. Banthorpe, E. D. Hughes and C. Ingold, *ibid.*, 4054 (1960); (f) E. D. Hughes and J. Wilby, *ibid.*, 4094 (1960); (g) V. J. Shriner, Jr., and M. L. Smith, *J. Am. Chem. Soc.*, **80**, 4095 (1958); (h) W. H. Saunders, Jr., and D. H. Edison, *ibid.*, **82**, 138 (1960); (i) S. J. Cristol and R. S. Bly, Jr., *ibid.*, **82**, 142 (1960); (j) W. H. Saunders, Jr., and R. A. Williams, *ibid.*, **79**, 3712 (1957).

the extent of C–X breaking may be greater or less than of C–H breaking at the transition state.

A small hydrogen isotope effect indicates that the hydrogen atom is, at the transition state, either very slightly or very extensively transferred to the base which receives it.[41] It follows that an E2 mechanism may demonstrate a small hydrogen isotope effect if C–H rupture is either far ahead of or far behind C–X rupture. In the present case, noting that $C_\alpha$ of RCl is tertiary, we judge the mechanism to be one with C–X breaking in the lead; that is, an E2 mechanism leaning toward the E1. The transition state may be sketched as VIII. The faint dotted lines stand for bonds largely broken (a) or but slightly formed (b and d),



VIII

and the heavy dashed line for a bond (c) only slightly disrupted.

The small β-phenyl substituent effect is consistent with transition state VIII, though not as definitive as the hydrogen isotope effect. The familiar activating effect of β-phenyl stems from either or both (a) conjugative interaction with the developing double bond[33] and (b) mesomeric stabilization of negative charge on $C_\beta$.[40c,j] The first should be of small and the second of no importance in the transition state proposed.

The reason the small β-phenyl substituent effect is not definitive is that steric effects within a "fully synchronous" E2 transition state would operate in the same direction. In II, the phenyl group is necessarily *cis* to a methyl group. In a fully synchronous transition state, the approach of phenyl to methyl would create compressions and would, moreover, tilt the phenyl group so as to interfere with its conjugation with the developing double bond. Neither effect is present in the transition state for elimination from β-phenylethyl bromide. On the other hand, neither effect should be serious in transition state VIII.

**Comparison of Reagents.**—That $NaSC_2H_5$ is some 7.5-fold more effective than $NaOCH_3$ in effecting elimination from RCl and $R_DCl$ is deduced from comparison of slopes in Figs. 1 and 2. Similar observations have been made by de la Mare and Vernon[32] and by Eliel and co-workers.[42] It appears that mercaptide reagents are stronger bases in the kinetic sense than are alkoxide ions, though weaker bases thermodynamically. The same inversion between kinetic and thermodynamic strengths has been noted with respect to reactions at carbon.[43]

Winstein, Darwish and Holness[44] proposed an extraordinary "merged" substitution–elimination mechanism to account for elimination from *trans*-4-*t*-butylcyclohexyl *p*-toluenesulfonate induced by halide ions in acetone solution. Eliel[42b,45] has embraced this mechanism to explain the substantial fraction of elimination from reactions of several cyclohexyl tosylates and bromides with sodium thiophenoxide. We see no need to invoke the "merged" mechanism to account for our results. Presumably it would call for some substitution to accompany elimination, but we found no substitution product containing the thioethoxy group. Indeed, we are not convinced that the "merged" mechanism is required for any of the reactions to which it has been applied.

That slopes in Figs. 1 and 2 for sodium perchlorate are higher than for sodium methoxide is a consequence, we think, of sodium perchlorate having a high positive salt effect on the $S_N1$–E1 solvolysis reaction, while sodium methoxide has a low salt effect (perhaps even negative[35]) on solvolysis and a rather small E2 rate coefficient. Evidence that the reaction in the presence of sodium perchlorate is substantially the same as the pure solvolysis is the near-identity of the product proportions (Table IV) and of the over-all hydrogen isotope effects. The over-all solvolysis isotope effect, $k_H/k_D$, is the ratio of intercepts in Figs. 1 and 2, namely 1.13, and over-all $k_H/k_D$ for the perchlorate-accelerated part of the reaction is the ratio of the relevant slopes, 1.26. With an eye to the rather large average deviation of the intercept in Fig. 1, we consider these ratios to be not significantly different.

**The Solvolysis Reaction.**—The antithetical possibilities of β-phenyl participation in a unimolecular process, and of a bimolecular mechanism, must be considered.

Neighboring group participation by the β-phenyl group can be counted out on grounds of observations and theory due to Winstein and coworkers. Solvolysis of 1-phenyl-2-propyl *p*-toluenesulfonate, a secondary analog of our tertiary RCl, was judged from rates and stereochemistry to involve very little phenyl participation.[46] The increased α-substitution in our RCl should further discourage participation.[47] The rate of methanolysis of RCl at 75.8° ($1.38 \times 10^{-4}$ sec.$^{-1}$) is 0.35 that of *t*-butyl chloride at the same temperature ($3.9 \times 10^{-4}$ sec.$^{-1}$) as extrapolated from data of Winstein and Fainberg.[48] The β-phenyl group, with its electron-attracting inductvie effect, would be expected to decelerate heterolysis to an open carbonium ion.

Our data are not sufficient to exclude all traces of bimolecular character from the solvolysis reaction. An E2 mechanism in which C–Cl scission was nearly complete at the transition state, accompanied by an $S_N2$ mechanism in which C–Cl was nearly sundered and C–O but slightly formed, would possibly show the isotope and salt effects observed. Nor are the data adequate to tell

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(41) F. H. Westheimer, *Chem. Revs.*, **61**, 265 (1961).

(42) (a) E. L. Eliel and R. S. Ro, *J. Am. Chem. Soc.*, **79**, 5995 (1957); (b) E. L. Eliel and R. G. Haber, *ibid.*, **81**, 1249 (1959).

(43) J. F. Bunnett, C. F. Hauser and K. V. Nahabedian, *Proc. Chem. Soc.*, 305 (1961).

(44) S. Winstein, D. Darwish and N. J. Holness, *J. Am. Chem. Soc.*, **78**, 2915 (1956).

(45) E. L. Eliel and R. S. Ro, *Tetrahedron*, **2**, 353 (1958).

(46) S. Winstein, M. Brown, K. C. Schreiber and A. H. Schlesinger, *J. Am. Chem. Soc.*, **74**, 1140 (1952).

(47) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber and J. Corse, *ibid.*, **74**, 1113 (1952).

(48) S. Winstein and A. H. Fainberg, *ibid.*, **79**, 5937 (1957)

whether the solvolysis product is formed from the attack of solvent on free carbonium ions or on ion pairs.

**The possibility that all reactions are unimolecular** can be excluded. Were it so, the slopes in Figs. 1 and 2 would all represent salt effects on the initial heterolysis and the changes in product composition (Table IV) would stem from the several bases (nucleophiles) giving rise to different product proportions in reaction with $R^+$ or $R_D^+$. The consistency of the dissection of rates and products (Table VI) would be the consequence of a fortuitous matching of the two effects.

The all-unimolecular model would call for over-all $k_H/k_D$ ratios to be independent of the reagent employed; the proportionate acceleration by a salt should not depend on what hydrogen isotope is present on β-carbons. We have seen that $k_H/k_D$ for pure solvolysis (1.13) is within experimental error the same as for the perchlorate-accelerated part of the reaction (1.26). But for the methoxide- and thioethoxide-accelerated parts, $k_H/k_D$ (that is, the ratios of corresponding slopes in Figs. 1 and 2) are both 1.86. The difference from 1.13 or 1.26 is much greater than experimental error. The all-unimolecular model fails.

A further test is the experiment behind Fig. 3. Pure unimolecular solvolysis in the presence of varying concentrations of $NaClO_4$ but a constant concentration of $NaOCH_3$ should give products of *constant* composition because the rates of product-forming reactions should be proportional only to the concentrations of product-forming reagents. This expectation is represented by line A in Fig. 3. From Table IV, it is clear that large concentrations of $NaClO_4$ do not affect the proportion in which products are formed. On the other hand, a mixture of solvolysis (including that accelerated by $NaClO_4$) and E2 reaction with $NaOCH_3$ should give varying yields of II represented by dashed line C; this line was constructed from rate and product information in Tables II and IV. The actual product ratios are closer to those predicted on the latter model.[49]

Another mechanistic model, in which the bimolecular eliminations occur *via* attack of $CH_3O^-$ or $C_2H_5S^-$ on ion pairs in mobile equilibrium with RCl or $R_DCl$, is compatible with the kinetics, but probably does not account for the hydrogen isotope effects. On this model, II or III would be formed in solvolysis by the same kind of process as in reactions with the anionic bases: attack of the base on the ion pair. One presumes that the transition state would be attained earlier in reactions with the stronger bases, with consequent lowering of the isotope effect. The *partial* $k_H/k_D$, pertaining only to formation of II, in solvolysis is computed from yield and product data to be 1.9. In reactions with the stronger bases (see above) it is 2.4 and 2.6. The facts are contrary to predictions from the model.

On the other hand, the model of mixed E1–$S_N1$ + E2 gives a good account of these ratios: $R^+$, being a high energy species, arrives at the transition state much sooner as it transfers a proton to methanol than does the less energetic RCl in reaction with the anionic bases.[50]

**Relation of the Present to Other Elimination Reactions.**—Most of the other recent research[40] revealing the lack of complete synchroneity in E2 reactions has dealt with mechanisms in which $C_\beta$–H severance is advanced over $C_\alpha$–X rupture at the transition state. The reactions described in this paper lie near the other extreme of the E2 mechanism, leaning strongly toward the E1. Some of the reactions of Cram, Greene and DePuy[40a] also lie on the E1 side.

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(49) That yields of II are slightly higher than predicted may again be due to shortcomings in the assumptions involved (the above-numbered assumptions 1 and 2). We suspect that assumption 2 is the principal culprit.[34]

(50) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).