Thermal Isomerizations of Some Chlorine-Substituted Vinylcyclopropanes

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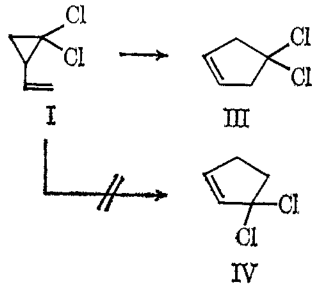
The isomerization at 200–300° of a number of chlorine-substituted vinylcyclopropanes is described. 1,1-Dichloro-2-vinylcyclopropane yields 4,4-dichlorocyclopentene, 1,1-dichloro-2-methyl-2-vinylcyclopropane yields 1-methyl-4,4-dichlorocyclopentene, and 7,7-dichlorobicyclo[4.1.0]hept-2-ene yields 4-dichloromethylenecyclohexene and benzyl chloride. 1,1-Dichloro-2-cyclopropylprop-1-ene and the isomers of 1-chloro-2-cyclopropylprop-1-ene, however, are stable up to 400°. Above this temperature, extensive decomposition occurs to give mainly polymer. The implications of these observations are discussed.

The rearrangements of vinylcyclopropanes to cyclopentenes are generally considered to be "valence isomerizations" in which bond breaking, bond making, and migration of the double bond are essentially synchronous.[1] It has been suggested that substitution of groups capable of stabilizing free radicals on the carbon atoms involved in this type of rearrangement may cause the reaction to follow a free-radical route.[2]

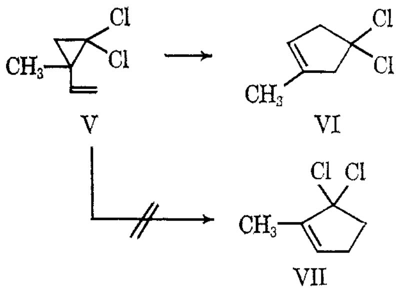
Such a compound is 1,1-dichloro-2-vinylcyclopropane (I), the pyrolysis of which has been described.[3] However, the results are difficult to interpret mechanistically, since the major component of the complex product mixture is monochlorocyclopentadiene (II). Compound II is presumed to have formed by dehydrochlorination of 4,4-dichlorocyclopentene (III), which may result either from a valence isomerization or arrangement *via* a diradical intermediate of compound I.

Since this pyrolysis was carried out at 475–500°, temperatures at which III might well be unstable, it seemed desirable to study the reaction at lower temperatures. Neureiter, however, has reported that no reaction takes place at 300° or below under the conditions of his experiments.[3] Nevertheless, by employing longer residence times we have been able to study this and similar reactions at 200–275°.

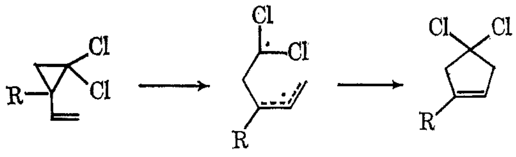
At 200°, I gave exclusively 4,4-dichlorocyclopentene (III). No 3,3-dichlorocyclopentene (IV) was found, even in trace quantities. Up to 275°, III is the only liquid product present. However, polymer formation, negligible at 200°, becomes increasingly evident as the temperature is raised. The precise structure of this polymer could not be determined. It gave the correct analysis for $(C_5H_4Cl)_x$; consequently HCl is eliminated during its formation. Above 275°, liquid products other than III are found and our observations are in accord with those of Neureiter.

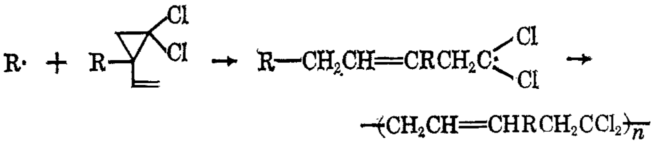

I III IV

The pyrolysis of 1,1-dichloro-2-methyl-2-vinylcyclopropane (V) at 200–275° likewise yields exclusively 1-methyl-4,4-dichlorocyclopentene (VI). No 2-methyl-3,3-dichlorocyclopentene (VII) was found. Some polymer formation occurred at the higher temperature to give material of empirical formula $(C_6H_7Cl)_x$.


V VI VII

The exclusive formation of the cyclopentenes corresponding to the expected diradicals from I and V supports Breslow's view that the chlorine substituents stabilize such intermediates in these rearrangements which, consequently, may not involve simultaneous bond breaking and bond making. Polymer formation may occur by attack of the diradical or other radical species upon I and V to give VIII.[4] This polymer would probably thermally degrade in the manner of polyvinylchloride to a material having the observed composition.[5]


R = H, CH_3


VIII

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[1] W. v. E. Doering and W. R. Roth, *Angew. Chem. Intern. Ed. Engl.*, **2**, 115 (1963).

[2] R. Breslow, "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p. 236.

[3] N. P. Neureiter, *J. Org. Chem.*, **24**, 2044 (1959).

[4] T. Takahashi, I. Yamashita, and T. Miyakawa, *Bull. Chem. Soc. Japan*, **37**, 131 (1964).

[5] For a review of polyvinyl chloride degradation, see F. Chevassus and R. de Broutelles, "The Stabilization of Polyvinylchloride," St. Martin Press, New York, N. Y., 1963.

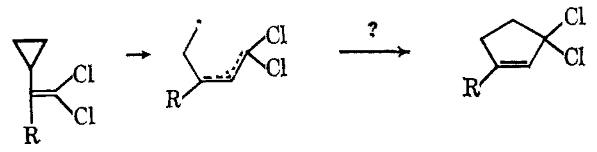
The rearrangements of both I and V give good first-order rate plots. In Table I, the rate constants for the rearrangement of compound V are compared with part of the data obtained by Frey and Marshall for the corresponding nonchlorinated compound.[6] The rates are much higher for the chlorinated compounds, k_1 for the rearrangement of V at 200°, for example, being about equal to that extrapolated for 2-cyclopropylpropene at 340°. Consequently, the ability of the chlorine substituents to stabilize the diradical must also provide a strong driving force for the rearrangements of I and V.

TABLE I

Compound	$10^5 k_1$, sec.$^{-1}$ (temp., °C.)		
1-Methyl-1-vinyl-2,2-dichlorocyclopropane	6.5 (200)	16.2 (212)	50.2 (234)
Isopropenylcyclopropane	8.3 (346)	17.0 (357)	42.4 (371)

The rate data show no evidence of inhibition by product. Since both IV and VI might, like methylcyclopentene, be expected to be powerful radical inhibitors, this is curious.[7] Furthermore, added oxygen has no effect upon the rates of disappearance of I and V. Possibly intramolecular radical coupling to the five-membered ring is so favored and so rapid that inhibition by radical traps does not occur.

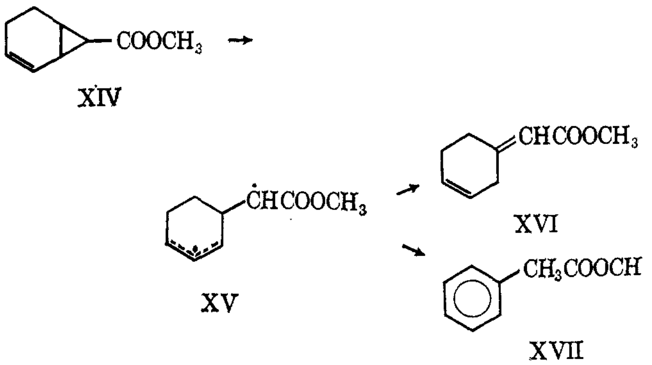
Substitution of chlorine on the 2-carbon of the vinyl group of 1-cyclopropylethylenes IX would further stabilize the allylic end of a diradical intermediate.

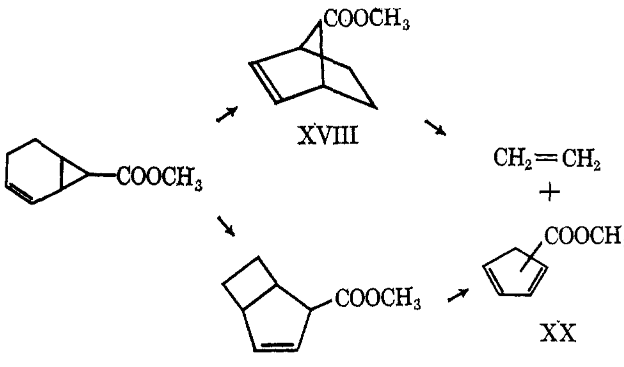

IX X

Rather than ring closure, intermolecular coupling of the reactive $-\dot{C}H_2$ ends of the radicals (X) might occur. To test this possibility, 1,1-dichloro-2-cyclopropylprop-1-ene (XI) was pyrolyzed by passing through a heated, glass wool packed column. Compound XI proved to be remarkably stable, showing no change in its n.m.r. spectrum up to 400°. At 450°, however, XI rapidly decomposed to give at least 16 products. The major product, contaminated with about 5% of another material, was isolated from the mixture and appeared, from n.m.r. and infrared data, to be 1,1-dichloro-2-methylpenta-1,4-diene (XII). Approximately 50% of the starting material was converted to a deep blue polymer. Introduction of two electron-withdrawing groups on the terminal carbon of the double bond apparently reduces the participation of the π electrons in the opening of the cyclopropyl ring so that simple thermal rupture of the ring, a reaction having a considerably higher activation energy than that found normally for the rearrangements of vinylcyclopropanes, must predominate in this case.[6] Our failure to find any substantial amounts of either 1,1-dichloro-2-methylpenta-1,3-diene or 1,1-dichloro-2,3-dimethylbuta-1,4-diene may have been due to polymerization of these conjugated dienes.

We have recently shown that a vinyl methyl group *cis* to a cyclopropyl group greatly reduces the rate of thermal rearrangement of a 1-propenylcyclopropane and also leads to the formation of polymeric products, whereas a methyl group *trans* to cyclopropyl has no effect.[8] An alternative explanation for the failure of XI to undergo rearrangement at "normal" temperatures could therefore be steric inhibition by the chlorine atom *cis* to cyclopropyl. To check this possibility, 1-chloro-2-cyclopropylprop-1-ene (XIII) was synthesized and separated by preparative v.p.c. into its *cis* and *trans* isomers. Neither isomer gave any reaction when heated in sealed tubes for 4 hr. at 350°. Above 400°, both isomers reacted at the same rate to give exclusively polymeric material. The effect of the chlorine substituents in these compounds is therefore polar rather than steric.

Berson has studied in considerable detail the thermal rearrangements at 425° of the isomeric 7-carbomethoxy-[4.1.0]hept-2-enes (XIV) in which the vinylcyclopropane system is incorporated in a fused ring.[9] To explain the relatively large number of products observed, three major mechanistic routes were proposed: (1) cleavage at C-1–C-7 to give a diradical, XV, which yields compounds XVI and XVII; (2) vinylcyclopropane-type rearrangements to either XVIII or XIX, which are not detected but are assumed to be precursors of the found products, ethylene and carbomethoxycyclopentadiene (XX); and (3) the formation of a heptatrienecarboxylic ester which can cyclize to methyl-substituted toluic esters. The substitution of two chlorine groups for carbomethoxy should certainly favor mechanistic route 1 over 2 and possibly 3. In agreement with this, 7,7-dichlorobicyclo[4.1.0]-


XIV XV XVI XVII


XVIII XIX XX

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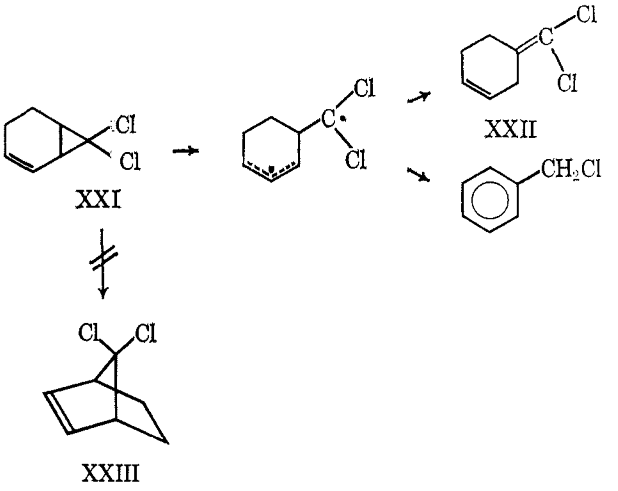
(6) H. M. Frey and D. C. Marshall, *J. Chem. Soc.*, 3981 (1962).

(7) H. M. Frey and M. C. Flowers, *ibid.*, 3547 (1961).

(8) A. J. Berlin, L. P. Fisher, and A. D. Ketley, *Chem. Ind.* (London), 509 (1965).

(9) J. A. Berson and E. S. Hand, *J. Am. Chem Soc.*, **86**, 1978 (1964).

hept-2-ene (XXI) was found to give only two products, other than trace polymer, when pyrolyzed at 275°: benzyl chloride (36%) and 4-dichloromethylenecyclohexene (XXII) (64%). Neither the expected product from a vinylcyclopropane rearrangement, 7,7-dichlorobicyclo[2.2.1]hept-2-ene (XXIII), nor any ethylene and dichlorocyclopentadiene was found in the pyrolysate. Chlorotoluenes formed by route 3, if present, constituted less than 1% of the product. Two analogous reactions, the rearrangements of 6,6-dichlorobicyclo[3.1.0]hex-3-ene (XXIV) and 8,8-dichlorobicyclo[5.1.0]octa-2,4-diene (XXV) have been reported by ter Borg and Bickel.[10] However, only the aromatic product is formed, XXIV giving chlorobenzene and XXV giving 1-chlorobenzocyclobutene. Apparently a 1,2 hydrogen shift such as occurs in the formation of XXII is much less favored when the resulting product contains a five- or seven-membered ring.



Experimental Section

1,1-Dichloro-2-vinylcyclopropane (I).—Potassium *t*-butoxide (160 g.) was added to 1200 ml. of *n*-pentane cooled to −24°. Buta-1,3-diene (239 g.) was distilled into the flask through a sodium hydroxide drying tower. Chloroform (170 g.) was then added dropwise at a rate such that the reaction temperature did not rise above −10°. After addition was complete, the reaction mixture was stirred for 1 hr. and then allowed to come to room temperature. The solution was washed with dilute hydrochloric acid, then water, after which the organic layer was separated and dried. Distillation yielded 92.5 g. of I, b.p. 125° (750 mm.), $n^{20}\text{D}$ 1.4733. The infrared spectrum showed bands at 6.32 (C=C stretch) and 9.80 μ (cyclopropyl). Other bands were at 6.91, 7.53, 7.81, 7.95, 8.46, 9.77, 11.20, 12.42, and 14.24 μ.

Anal. Calcd. for $C_5H_6Cl_2$: C, 43.80; H, 4.37; Cl, 51.83. Found: C, 43.83; H, 4.44; Cl, 51.84.

4,4-Dichlorocyclopent-1-ene (III).—1,1-Dichloro-2-vinylcyclopropane (15 g.) was passed during 1 hr. in a stream of nitrogen through a 1-m. Vycor tube packed with glass wool and heated to 250°. The product was collected in an ice-cooled flask and returned to the column. This procedure, repeated five times, yielded a 77% yield of III which was separated from unreacted starting material by preparative v.p.c. The n.m.r. spectrum of III showed a very sharp methylene signal at τ 6.82 (relative area 2) and a sharp olefinic proton signal at τ 4.48 (relative area 1). The *J* values for coupling between protons on carbons 1 and 2 and carbons 1 and 3 are apparently of equal magnitude but opposite sign. This has been observed to be the case with a number of other materials of structure $\overline{XCH_2CH{=}CHCH_2}$ where X contains no protons.[11]

Anal. Calcd. for $C_5H_6Cl_2$: C, 43.80; H, 4.37; Cl, 51.83. Found: C, 43.84; H, 4.41; Cl, 51.71.

1,1-Dichloro-2-methyl-2-vinylcyclopropane (V).—Potassium *t*-butoxide (196 g.) was added to 1500 ml. of *n*-pentane cooled to −18° after which isoprene (140 ml.) was distilled in through a sodium hydroxide drying tower. Chloroform (140 ml.) was then added dropwise at such a rate that the temperature of the reaction mixture did not rise above −10°. After addition was complete, the reaction mixture was stirred for 1 hr. and then allowed to come to room temperature. The solution was washed with dilute hydrochloric acid, then water, after which the organic layer was separated and dried. Distillation yielded 48.5 g. of V, b.p. 60° (38 mm.), $n^{20}\text{D}$ 1.4787. The infrared spectrum showed bands at 6.18 (C=C stretch) and 9.91 μ (cyclopropyl). Other bands appeared at 3.21, 3.33, 5.46, 6.90, 7.18, 7.50, 7.75, 9.26, 9.52, 10.87, 11.91, 12.53, 14.0, and 14.68 μ.

Anal. Calcd. for $C_6H_8Cl_2$: C, 47.67; H, 5.30; Cl, 47.03. Found: C, 47.79; H, 5.43; Cl, 46.78.

1-Methyl-4,4-dichlorocyclopentene (VI).—Compound V was pyrolyzed in an identical manner with compound I above. An 84% yield of VI was obtained, separation from unreacted V being accomplished by preparative v.p.c. The infrared spectrum of VI showed bands at 6.18 (C=C stretch) and 12.52 μ (C–Cl). Other bands were at 5.75, 6.13, 7.01, 7.28, 7.50, 7.75, 8.18, 9.63, 9.81, and 10.55 μ. The n.m.r. spectrum of VI consisted of a sharp methyl signal at τ 8.32 (relative area 3), a methylene multiplet at τ 6.95 (relative area 4), and a triplet for the olefinic proton centered at τ 4.89 (relative area 1).

Anal. Calcd. for $C_6H_8Cl_2$: C, 47.67; H, 5.30; Cl, 47.03. Found: C, 47.79; H, 5.46; Cl, 47.05.

1,1-Dichloro-2-cyclopropylpropene (XI).—Triphenylphosphine (222 g.) was dissolved in 475 ml. of anhydrous carbon tetrachloride and heated to 60°. Methylcyclopropyl ketone (71.3 g.) was then added and the reaction was stirred at 60° for 3.5 hr. Water (200 ml.) was added to the cooled mixture and, after shaking, the aqueous and nonaqueous phases were separated. The aqueous layer was extracted twice with 100-ml. portions of ether, and these extracts were added to the organic phase. The combined organic material was dried over anhydrous magnesium sulfate and then distilled. Compound XI (25.0 g) distilled at 121° (200 mm.). The infrared spectrum showed bands at 6.23 (C=C stretch) and 9.53 μ (cyclopropyl). Other bands were at 7.21, 7.94, 9.18, 9.53, 9.63, 9.87, 10.60, 11.11, and 12.23 μ. The n.m.r. spectrum of XI consists of a multiplet for cyclopropyl CH_2 centered at τ 9.42 (relative area 4), a multiplet for cyclopropyl CH centered at τ 7.98 (relative area 1), and a sharp methyl singlet at τ 8.47 (relative area 3).

Anal. Calcd. for $C_6H_8Cl_2$: C, 47.67; H, 5.30; Cl 47.03. Found: C, 47.80; H, 5.60; Cl 47.27.

1,1-Dichloro-2-methylpenta-1,4-diene (XII).—1,1-Dichloro-2-cyclopropylpropane (5 ml.) was passed slowly through a Vycor tube packed with glass wool and held at 455°. A deep blue liquid (4.65 ml.) was collected. All liquid products were removed from polymer on a vacuum line. Compound XII was isolated from the resulting mixture by preparative v.p.c. on a Ucon oil column. The v.p.c. of compound XII on an analytical instrument showed a shoulder on the main peak corresponding to probably about 5% impurity. It was not possible to remove this material by preparative v.p.c. The infrared spectrum showed two separate carbon–carbon stretching peaks at 6.35 and 6.20 μ. Other bands were at 3.31, 6.83, 7.28, 8.10, 8.37, 9.62, 10.25, 11.01, and 14.73 μ. The n.m.r. spectrum consisted of a methyl singlet at τ 8.22 (relative area 3), a methylene doublet at τ 7.05 (relative area 2), and a multiplet for the vinyl protons centered at τ 4.68 (relative area 3).

Anal. Calcd. for $C_6H_8Cl_2$: C, 47.67; H, 5.30; Cl, 47.03. Found: C, 49.18; H, 5.55; Cl, 45.09.

1-Chloro-2-cyclopropylprop-1-ene (XIII).—Triphenylphosphine (263 g.) and paraformaldehyde (90 g.) were suspended in 500 ml. of anhydrous ether. Dry HCl gas was then bubbled through for 2 hr. The resulting white solid was collected and purified by dissolving in methylene chloride and reprecipitating with ether. The product was dissolved again in methylene chloride and heated for 1 hr. with thionyl choride (177 g.). Volatile products were stripped off under vacuum and the residue was dissolved in hot methylene chloride and then reprecipitated with ethyl acetate. After drying, 21 g. of this material (m.p. 260–261°) was dissolved in 50 ml. of ether and the solution was cooled to −30°. *n*-Butyllithium (7.1 g.) in *n*-hexane (10 ml.) and ether (50 ml.) was added, and the mixture was stirred for

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[10] A. P. ter Borg and A. F. Bickel, *Proc. Chem. Soc.*, 283 (1958).

[11] B. L. Shapiro, personal communication.

0.5 hr. Methylcyclopropyl ketone (8.4 g.) in 25 ml. of ether was then added and stirring was continued for 1 hr. more. The reaction was mixed with 150 ml. of water and the ether layer was then separated and dried. Distillation yielded 1.5 g. of XIII, b.p. 50° (43 mm.). The infrared spectrum showed a carbon–carbon stretching band at 6.22 μ and a cyclopropyl band at 9.51 μ. Other bands were at 3.25, 3.41, 3.72, 4.77, 5.23, 7.01, 7.48, 8.28, 8.64, 9.51, and 12.50 μ. Compound XIII was separated into its *cis* and *trans* isomers using preparative v.p.c. (Ucon oil column). The n.m.r. spectrum of one isomer consisted of a multiplet for cyclopropyl CH_2 centered at τ 9.37 (relative area 4), a methyl singlet at τ 8.60 (relative area 3), and a broad peak for the vinyl proton at τ 4.28 (relative area 1). The n.m.r. spectrum of the other isomer likewise consisted of a multiplet centered at τ 9.49, a singlet at τ 8.36, and a broad peak at τ 4.25 (relative areas 4:3:1). No attempt was made to assign which isomer was *cis* and which was *trans*. The infrared spectrum of each isomer was indistinguishable from the mixture of the two.

Anal. Calcd. for C_6H_9Cl: C, 61.78; H, 7.73; Cl, 30.49. Found: C, 61.71; H, 7.87; Cl, 30.26.

7,7-Dichlorobicyclo[4.1.0]hept-2-ene (XXI).—Potassium *t*-butoxide (33.7 g.) was slurried in 500 ml. of dry *n*-pentane containing 46.2 g. of cyclohexa-1,3-diene. The mixture was cooled in an ice–salt bath, and chloroform (34.6 g.) was added dropwise over a 2-hr. period, the temperature being kept below 0°. The reaction mixture was then warmed to room temperature and washed with dilute hydrochloric acid. The organic layer was separated, washed with water, dried, and distilled. Compound XXI (18.5 g.) was obtained as a colorless, sweet-smelling liquid, b.p. 65° (5.5 mm.). The infrared spectrum of XXI showed bands at 6.00 (C=C stretch) and 9.53 μ (cyclopropyl). Other bands were at 3.42, 6.20, 7.05, 7.22, 7.71, 8.18, 10.25, 11.89, 12.20, and 13.65 μ. The n.m.r. spectrum of this material consists of multiplets centered at τ 8.78 (cyclopropyl CH), 7.82 (methylene CH_2), 7.02 (allylic CH_2), and 3.98 (vinyl). All four groups of signals have approximately the same areas.

Anal. Calcd. for $C_7H_8Cl_2$: C, 51.53; H, 4.91; Cl, 43.56. Found: C, 51.53; H, 4.88; Cl, 43.58.

4-Dichloromethylenecyclohexene (XXII).—Compound XXI was passed through a 1-m. Vycor tube packed with glass wool and held at 275°, 18 times at a rate of 30 ml./hr. The product showed only two major peaks in the v.p.c. These two materials were separated by preparative v.p.c. on a Ucon oil column. One was shown, by comparison with an authentic sample, to be benzyl chloride. The other was shown to be compound XXII. The infrared spectrum of XXII consisted of a carbon–carbon stretching absorption at 6.32 μ and other bands at 3.41, 6.33, 7.14, 7.42, 7.68, 8.01, 8.24, 9.53, 10.18, and 12.20 μ. The n.m.r. spectrum of XXII consisted of a multiplet for methylene protons centered at τ 8.15 (relative area 3) and an olefinic proton signal centered at τ 4.33 (relative area 1).

Anal. Calcd. for $C_7H_8Cl_2$: C, 51.53; H, 4.91; Cl, 43.56. Found: C, 51.47; H, 4.90; Cl, 43.64

Kinetic Measurements.—Samples (0.5 ml.) of compounds I or V were placed in 25-ml. Pyrex ampoules and thoroughly degassed on a vacuum line at $<10^{-6}$ mm. They were then sealed at $<10^{-6}$ mm. and placed in a furnace held at ±1° of the reaction temperature by an electronic controller. Sample tubes were removed at 15-min. intervals and quenched in a stream of compressed air after which they were analyzed by v.p.c. Products obtained in this way were shown to be identical with those obtained by pyrolysis in open tubes.

Analogs of Neuroeffectors. V.

Neighboring-Group Effects in the Reactions of Esters, Thiolesters, and Selenolesters. The Hydrolysis and Aminolysis of Benzoylcholine, Benzoylthiolcholine, Benzoylselenolcholine, and of Their Dimethylamino Analogs[1]

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To obtain information about the relative importance of neighboring-group effects in the reactions of isologous esters, thiolesters, and selenolesters, a study of the aminolysis and hydrolysis of 2-dimethylaminoethyl benzoate, 2-dimethylaminoethyl thiolbenzoate, 2-dimethylaminoethyl selenolbenzoate, benzoyl choline, benzoyl thiolcholine, and benzoyl selenolcholine was carried out. Aminolysis rates increased sharply from ester to thiolester to selenolester. Tertiary and quaternary analogs reacted with *n*-butylamine at essentially identical rates. The three choline isologs underwent hydrolysis at rather similar rates, the order of reactivity being selenolester > ester > thiolester. Below a pH of 8 the ability of the selenolester and, to a lesser extent, of the thiolester to interact with phosphate became kinetically significant. For the tertiary amino compounds, plots of pH against log k_{obsd} yielded sigmoid curves from which the dissociation constants of the dimethylammonium groups could be derived. Anchimeric assistance by the dimethylamino group accelerated the reaction rates of all the tertiary amino compounds above those of the choline analogs below a pH of 11; this effect was more pronounced for the thiolester and selenolester than for the ester. Nucleophilic catalysis rather than general acid–specific base catalysis appears to be involved as suggested by the observation that the relative order of hydrolysis, selenolester faster than thiolester faster than ester, is that previously noted for the aminolysis and different from that normally noted for the hydrolysis of such isologs. At pH values above 11, the tertiary amino compounds underwent hydrolysis more slowly than their quaternary analogs.

Since the recognition of the crucial metabolic roles played by thioacyl derivatives of coezyme A[2] in biological systems, a great deal of attention has been centered on the comparative mechanisms of the reactions of thiolesters[3–11] and of esters. It was noted that, while hydrolysis rates were affected relatively little when the oxygen of esters was replaced by sulfur,

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[1] This work was supported, in part, by grants from the National Science Foundation (GB-1626) and the National Cancer Institute of the U. S. Public Health Service (CA-3937-07).

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