Elimination Reactions of α-Halogenated Ketones. X.[1a] Extent of Concurrent Substitution Reaction Accompanying Chloride Ion-promoted Elimination from 2-Benzyl-2-halogeno-4,4-dimethyl-1-tetralones in Solvent Acetonitrile

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Previous communications have reported upon the bromide ion[2]- and chloride ion[3]-promoted elimination from 2-benzyl-2-bromo-4,4-dimethyl-1-tetralone (I) in solvent acetonitrile to yield only the endocyclic α,β-unsaturated ketone, 2-benzyl-4,4-dimethyl-1-keto-1,4-dihydronaphthalene (II). In this investigation it is shown that chloride ion-promoted elimination from 2-benzyl-2-chloro-4,4-dimethyl-1-tetralone (III) also yields only the endocyclic α,β-unsaturated ketone II.

In bromide ion-promoted elimination from bromotetralone I any concurrent substitution would merely regenerate the bromotetralone and it was not possible to establish whether substitution accompanied elimination. The kinetic pattern of the chloride ion-promoted elimination from bromotetralone I showed that reaction could not involve a rapid substitution of chloride for bromide followed by elimination either from chlorotetralone III or from an equilibrium mixture of bromotetralone I and chlorotetralone III. In this investigation by use of radiochloride ion (Cl^{36}) it has been found possible to investigate directly the extent of substitution accompanying chloride ion-promoted elimination from both bromotetralone I and chlorotetralone III.

Although at complete reaction only endocyclic α,β-unsaturated ketone II is isolated, during the earlier stages of reaction substitution may initially accompany elimination only for the substitution product formed to undergo eventually also an elimination reaction. The reactions of radiochloride ion with bromotetralone I and with chlorotetralone III were stopped at partial reaction and the organic component of the reaction mixture isolated. The radioactivity incorporated into the organic component gave a direct measure of the amount of substitution accompanying elimination. For chloride ion-promoted elimination from bromotetralone I at 24.5° it was found that each act of substitution was accompanied by about 200 of elimination; this low value for the substitution–elimination ratio is consistent with the clean second-order kinetics previously observed for the elimination reaction.[3] For chloride ion-promoted elimination from chlorotetralone III at 90.6° it was found that each act of substitution was accompanied by about 59 of elimination.

Bunnett, Davis, and Tanida, in attacking the merged mechanism,[4] considered the absence of any substitution product in their systems to indicate that their elimination reactions followed an E2 rather than a merged substitution–elimination mechanism. This argument is fallacious since two reaction paths are available on either the merged mechanism or on the mixed E2–SN2 reaction scheme. Although in general substitution will accompany elimination on either scheme, in practice many instances will occur in which one reaction path is sufficiently favored as for it to swamp out the alternative. This has long been recognized for the mixed E2–SN2 reaction scheme and identical arguments must hold for the merged substitution–elimination scheme. In the elimination reactions discussed within this communication a small degree of substitution is indeed found to accompany elimination but we do not consider this to be a requisite of the merged substitution–elimination mechanism which has been previously proposed for these elimination reactions.[5]

The kinetics of the chloride ion-promoted elimination from chlorotetralone III have not previously been investigated. A brief investigation was carried out, and it was found that the kinetics were of second order, first order in chlorotetralone III and first order in tetraethylammonium chloride. The reaction was found to have a high activation energy of 24.6 kcal./mole, together with a counterbalancing high frequency factor of $10^{12.7}$ l. moles^{-1}sec.$^{-1}$.

Experimental

The concentrations reported in this paper are uncorrected for expansion of the solvent from room temperature to reaction temperature. Other entities quoted which are concentration dependent are similarly uncorrected.

Materials.—Preparation of 2-benzyl-2-bromo-4,4-dimethyl-1-tetralone[6] and of tetraethylammonium chloride[3] have previously been described. Tetraethylammonium radiochloride was prepared in the same manner as was tetraethylammonium chloride but using a solution of HCl^{36}. The acetonitrile was Matheson, Coleman and Bell spectroquality reagent.

2-Benzyl-2-chloro-4,4-dimethyl-1-tetralone (III).—A 12-g. (0.045 mole) sample of 2-benzyl-4,4-dimethyl-1-tetralone was dissolved in 50 ml. of chloroform. A 360-ml. portion of 0.125 *M* chlorine solution in chloroform was added over a period of 45 min., the reaction mixture being irradiated with ultraviolet light. The solution was allowed to stand for a further 10 min. and then evaporated under vacuum. Recrystallization from petroleum ether, b.p. 60–70°, yielded 11 g. of colorless crystals, m.p. 70–75°. Repeated recrystallization from petroleum ether gave pure chlorotetralone III, m.p. 77–78°; λ_{max} 256 mμ (ϵ 12,200); λ_{min} 228 mμ (ϵ, 2400); $\gamma_{C=O}$ 1694/86.

Anal. Calcd. for $C_{19}H_{19}OCl$: C, 76.36; H, 6.41; Cl, 11.87. Found: C, 76.36; H, 6.44; Cl, 11.82.

Elimination from Chlorotetralone III as Promoted by Tetraethylammonium Chloride.—A 50-ml. portion of an acetonitrile solution 0.0400 *M* in chlorotetralone III and 0.0470 *M* in tetraethylammonium chloride was maintained at 90.6° for 40 hr. Titration against standard sodium methoxide in the usual manner indicated that 94% of stoichiometrically possible acid formation had taken place. Recovered was 0.464 g. of crude product (98% yield), m.p. 109–110.5°. The crude product had infrared and ultraviolet spectra superimposable upon those of an authentic sample of the endocyclic α,β-unsaturated ketone II.[6] After recrystallization from methanol the m.p. was 110.5–112.5°; endocyclic α,β-unsaturated ketone, 113–114°.[6]

Radioactive Tracer Techniques.—Counting was performed using a Tracerlab "100 scaler" employing a T.G.C.2. mica end-window geiger tube operating at 1400 volts. Measurements were carried out employing a 1-ml. sample of an acetonitrile solution of

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[1] (a) For paper IX in this series, see B. D. Pearson, R. P. Ayer, and N. H. Cromwell, *J. Org. Chem.*, **27**, 3038 (1962); (b) to whom correspondence concerning this article should be addressed.

[2] D. N. Kevill and N. H. Cromwell, *J. Am. Chem. Soc.*, **83**, 3812 (1961).

[3] G. Coppens, D. N. Kevill, and N. H. Cromwell, *J. Org. Chem.*, **27**, 3299 (1962).

[4] J. F. Bunnett, G. T. Davis, and H. Tanida, *J. Am. Chem. Soc.*, **84**, 1606 (1962).

[5] D. N. Kevill and N. H. Cromwell, *ibid.*, **83**, 3815 (1961).

[6] A. Hassner and N. H. Cromwell, *ibid.*, **80**, 893 (1958).

the material to be counted, contained in a glass dish at a standard distance from the end-window. Immediately before and after each counting operation the background count was determined and the mean value subtracted from the observed count. The usual counting time was 10 min. and the readings were then corrected to number of counts per minute.

Radioactive Count of Pure Tetraethylammonium Radiochloride.—A 1-ml. sample of a 0.0286 M solution of NEt_4Cl^{36} in acetonitrile was counted by the above procedure. The over-all count was found to be 3075 counts per min., which after correction for the background count of 33 counts per min., gave an actual solution count of 3042 per min.

Extent of Exchange Accompanying Chloride Ion-promoted Elimination from Bromotetralone I.—A 50-ml. portion of an acetonitrile solution 0.0300 M in bromotetralone I and 0.0263 M in NEt_4Cl^{36} was maintained at 24.5° for 80 min. A 5-ml. sample was removed and found to require 5.50 ml. of 0.0090 M sodium methoxide for neutralization. The acid formation corresponded to 33% elimination. To the remainder of the solution petroleum ether was added and the solution washed well with water until the washings were found to be nonradioactive. The petroleum ether solution was then evaporated to dryness under reduced pressure. A solution containing 0.0180 g. of product per ml. of acetonitrile was counted by the standard technique. The actual count on the sample was found to be only 6.0 per min. The product was redissolved in petroleum ether and again washed well with water; a repeat of the above procedure then led to an actual count of 7.0 per min. showing the small count to be due to an actual incorporation of radiochlorine into the organic residue and not due to a trace of radiochloride ion impurity.

Since the radiochlorine count is extremely low we can to an excellent approximation assume the organic residue to be a mixture of bromotetralone I (contaminated with a trace of chlorotetralone III) and endocyclic α,β-unsaturated ketone II. To 0.0180 g. of residue was added a little acetonitrile and excess piperidine and the mixture allowed to stand for 24 hr. Then 30 ml. of acetone and excess nitric acid were added and the bromide ion concentration determined by potentiometric titration was equivalent to 3.68 ml. of 0.0100 M silver nitrate. This corresponds to a bromotetralone I mole fraction of 0.63 in excellent agreement with the 33% elimination as determined by acid titration.

The concentration of bromotetralone I in the counted solution was 0.0378 M and for a concentration of 0.0286 M the count would have been 4.9 per min. The percentage uptake of radiochlorine into the bromotetralone is therefore 4.9/3042 × 100%; *i.e.*, 0.16%. When 33% elimination has occurred the remaining bromotetralone I has 0.16% of its bromine atoms replaced by radiochlorine atoms and for every act of substitution about 200 of elimination have taken place.

Extent of Exchange Accompanying Chloride Ion-promoted Elimination from Chlorotetralone III.—A 60-ml. portion of solution 0.0167 M in chlorotetralone III and 0.0182 M in NEt_4Cl^{36} was maintained at 90.6° for 95 min. A 5-ml. portion was found to require 4.62 ml. of 0.00900 M sodium methoxide for neutralization. This corresponds to 50% elimination reaction having taken place. To the remainder of the solution petroleum ether was added and the solution water washed until the washings were nonradioactive. The petroleum ether solution was then evaporated to dryness under reduced pressure.

A solution containing 0.0170 g. of product per ml. of acetonitrile was counted by the standard technique. The actual count on the sample was found to be 20.9 per min. To 0.0173 g. of sample was added a little acetonitrile and excess piperidine; the solution was maintained at 90.6° for 24 hr. and then 30 ml. of acetone was added and the solution acidified with nitric acid. The chloride ion was found by potentiometric titration to be equivalent to 2.90 ml. of 0.0100 M silver nitrate; this corresponds to a chlorotetralone III mole fraction of 0.47, in excellent agreement with the 50% elimination as determined by acid titration.

The concentration of chlorotetralone III in the counted solution was 0.0290 M and the percentage of Cl^{36} present was 20.9/3042 × 100%; *i.e.*, 0.69%. In determining the amount of exchange allowance must be made for dilution of the Cl^{36} by hydrogen chloride eliminated from the chlorotetralone. At 50% elimination $[NEt_4Cl^{36}]$ is 0.0182 M and [HCl] is 0.00835 M. The true percentage of chlorine exchange is, therefore, $0.69[0.0182 + 0.00835/2]/0.0182$; *i.e.*, 0.85%. When 50% elimination has occured the remaining chlorotetralone III has 0.85% of its chlorine atoms exchanged with those present as chloride ion in solution and for every act of substitution 59 of elimination have taken place.

Kinetics of the Chloride Ion-promoted Elimination from Chlorotetralone III.—All runs were carried out by the sealed bulb technique using 5.05-ml. aliquots. Titration of acid production was in 30 ml. of acetone previously rendered neutral to lacmoid indicator, against a standard solution of sodium methoxide in methanol. One run was followed by potentiometric titration against standard silver nitrate in a titration medium consisting of 30 ml. of acetone containing about 1 ml. of 1 N nitric acid. A silver wire electrode and a potassium nitrate–agar bridge to a diptype calomel reference electrode were used.

Throughout each individual run the first-order rate coefficients with respect to chlorotetralone III fell in value as reaction proceeded. Such a fall was observed and discussed for the bromide ion-promoted elimination from bromotetralone I.[2]

TABLE I

INITIAL SECOND-ORDER RATE COEFFICIENTS, k_2, FOR ACID PRODUCTION IN THE REACTION OF 2-BENZYL-2-CHLORO-4,4-DIMETHYL-1-TETRALONE WITH TETRAETHYLAMMONIUM CHLORIDE IN SOLVENT ACETONITRILE

t, °C.	[Chlorotetralone]	$[NEt_4Cl]$	10^3k_2, l. moles^{-1} sec.$^{-1}$
61.3	0.0200	0.0769	0.45
75.5	.0100	.00398	2.01[a]
75.5	.0200	.00961	1.93
75.5	.0200	.0769	1.86
90.6	.0200	.00961	8.9

[a] Initial second-order rate coefficient for bromide ion production is 2.06×10^{-3} l. moles^{-1} sec.$^{-1}$; $k_2 = Ae^{-E/RT}$; $A = 10^{12.7}$ l. moles^{-1} sec.$^{-1}$; $E = 24.6$ kcal./mole.

An illustrative run is given below; the first-order rate coefficients, k_1 (sec.$^{-1}$), are with respect to chlorotetralone III.

TEMPERATURE: 90.6°; 5.05-ML. ALIQUOTS AT 24°; [CHLOROTETRALONE]: 0.0200 M; $[NEt_4Cl]$: 0.00961; TITERS ARE IN ML. OF 0.00900 M NAOME

Time, min.	0	10	20	30	40	50	60
Titer	0.25	0.76	1.20	1.60	1.97	2.30	2.58
10^5 k_1:	..	7.98	7.58	7.31	7.12	6.90	6.64

Initial k_1 is 8.55×10^{-5} sec.$^{-1}$, corresponding to an initial second-order rate coefficient of 8.9×10^{-3} l. moles^{-1} sec.$^{-1}$.

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Decomposition of Aryldiazonium Hexafluorophosphates in Tetramethylurea. A New Deamination Procedure

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Interest in this laboratory in the thermal decomposition of aryldiazonium hexafluorophosphates to the corresponding aromatic fluorocarbons[2] has led to the discovery of a new deamination procedure. It has

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[2] Kenneth G. Rutherford, William Redmond, and James Rigamonti, C. S. B., *J. Org. Chem.*, **26**, 5149 (1961).