Polymer XIII from Bis(2-butadienylmethyl) *m*-Xylylenedicarbamate and Benzidinebismaleimide.—A solution of 0.31 g. (0.00090 mole) of benzidinebismaleimide, 0.32 g. (0.00090 mole) of bis(2-butadienylmethyl) *m*-xylylenedicarbamate and 0.005 g. of *N*-phenyl-β-naphthylamine in 25 ml. of dimethylformamide was heated at 100° for 24 hr. After addition of the polymer solution to 700 ml. of ether, the precipitated polymer was removed by filtration and dried to yield 0.45 g. (72%) of the tan powdery polymer XIII, softening at 145–150°, with an intrinsic viscosity of 0.15.

Notes

Elimination Reactions of α-Halogenated Ketones. VIII.[1a] Efficiency of Chloride Ion and Perchlorate Ion in the Promotion of Dehydrobromination of 2-Benzyl-2-bromo-4,4-dimethyl-1-tetralone in Solvent Acetonitrile

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It has been shown in a previous communication[2] that addition of tetraethylammonium bromide to an acetonitrile solution of 2-benzyl-2-bromo-4,4-dimethyl-1-tetralone (I) leads to a facile second-order elimination reaction, yielding only the endocyclic α,β-unsaturated ketone, 2-benzyl-4,4-dimethyl-1-keto-1,4-dihydronaphthalene (II). Concurrent substitution would merely regenerate the bromotetralone I, and it was not established as to whether bromide ion exchange accompanied the elimination reaction. It has been found that an identical elimination reaction is promoted by the addition of chloride ions as tetraethylammonium chloride.

At 25.0° the chloride ion-promoted elimination reaction is 26 times faster than for that promoted by an identical concentration of bromide ions. At 37.0° the reaction yielded 100% olefin formation as measured by acid production and a 99% yield of the endocyclic α,β-unsaturated ketone II was isolated. No evidence for any accompanying 2-benzyl-2-chloro-4,4-dimethyl-1-tetralone (III) was obtained.

Throughout each individual run the integrated second-order rate coefficients, first order with respect to bromotetralone I and first order with respect to tetraethylammonium chloride were constant during the initial stages of reaction and it appears that each hydrogen ion eliminated removes from the reaction mixture one kinetically active chloride ion, presumably as undissociated hydrochloric acid. Since the bromide ions liberated are less reactive than chloride ions by a factor of 26, only during the later stages of each run would interference by bromide ions be discernible. The formation of hydrochloric acid rather than hydrobromic acid is consistent with the excess of chloride ions over bromide ions present during the initial stages of reaction and with the known stronger acidity of hydrobromic acid over hydrochloric acid in solvent acetonitrile.[3]

The majority of the runs were followed by determination of the acidity developed within the solution but in one instance a run was followed by determination of the increase in halide ion concentration. It was found that at a given temperature the initial second-order rate coefficients were identical, independent of whether the reaction was followed by determination of the development of acidity or the development of halide ion.

The constant value obtained for the initial second-order rate coefficient over a wide range of reactant concentrations (Table I), clearly shows that reaction cannot involve a rapid substitution of chloride for bromide followed by elimination either from the chlorotetralone III or from an equilibrium mixture of bromotetralone I and chlorotetralone III.

The frequency factor of $10^{11.4}$ l. mole^{-1} sec.$^{-1}$ is greater than for that for bromide ion-promoted elimination[2] of $10^{10.9}$ l. mole^{-1} sec.$^{-1}$ and the activation energy of 18.5 kcal./mole is lower than for bromide ion-promoted elimination of 19.7 kcal./mole. It can be seen that both frequency factor and activation energy considerations favor at a given temperature a higher rate for chloride ion-promoted elimination relative to that of bromide ion-promoted elimination.

An attempt to determine the relative rates of bromide ion- and chloride ion-promoted elimination in 87% aqueous ethanol failed; solvolysis of

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(1) (a) For paper VII in this series see D. N. Kevill, P. H. Hess, P. W. Foster, and N. H. Cromwell, *J. Am. Chem. Soc.*, **84**, 983 (1962); (b) To whom corresponding concerning this article should be addressed.

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

(3) I. M. Kolthoff, S. Bruckenstein, and M. K. Chantooni, Jr., *ibid.*, **83**, 3927 (1961).

TABLE I

Initial values for the second-order rate coefficients for bromide ion production, $k_2^{Br^-}$ (l. mole^{-1} sec.$^{-1}$), and for the second-order rate coefficients for acid production, $k_2^{H^+}$ (l. mole^{-1} sec.$^{-1}$), in the reaction of 2-benzyl-2-bromo-4,4-dimethyl-1-tetralone (I) with tetraethylammonium chloride in solvent acetonitrile at various temperatures, *t*. Some determinations were carried out in the presence of tetraethylammonium perchlorate.

t °C.	[Bromo-tetralone]	[NEt$_4$Cl]	[NEt$_4$ClO$_4$]	$10^2k_2^{Br^-}$	$10^2k_2^{H^+}$
1.9	0.0200	0.0430			0.051
1.9	.0100	.0490			.050
1.9	.0200	.0157	0.0580		.048
26.9	.0100	.0065			.83
26.9	.0200	.0100		0.80	
26.9	.0100	.0294			.82
36.0	.0100	.0078			2.12
36.0	.0050	.0162			1.92
36.0	.0172	.0162			2.09
36.0	.0100	.0157	.0580		1.73

$k_2 = Ae^{-E/RT}$. $A = 10^{11.4}$ l. mole^{-1} sec.; $E = 18.5$ kcal./mole.

the bromotetralone I was found to be the dominant reaction.

The differing rates of chloride ion- and of bromide ion-promoted elimination indicate very strongly that the ions are entering the transition state and are not merely accelerating the self-decomposition of the bromotetralone I in solvent acetonitrile through a powerful salt effect. That this is indeed the case was confirmed by the addition of 0.1140 *M* tetraethylammonium perchlorate to a 0.0100 *M* acetonitrile solution of the bromotetralone I at 60.0°. It was found that the rate of self-decomposition[2] was not appreciably altered by the presence of weakly nucleophilic perchlorate ions. Similarly, (Table I), it was found that the addition of excess tetraethylammonium perchlorate did not appreciably affect the rates of chloride ion-promoted elimination from the bromotetralone I.

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 the 2-benzyl-2-bromo-4,4-dimethyl-1-tetralone has previously been described.[4]

Tetraethylammonium chloride was prepared by the neutralization of an aqueous 10% solution of tetraethylammonium hydroxide with hydrochloric acid. The residue, after evaporation to dryness, was recrystallized from acetonitrile–acetone and dried under vacuum over phosphorus pentoxide. During the preparation of solutions the salt was manipulated within a nitrogen dry atmosphere.

Tetraethylammonium perchlorate was prepared by neutralizing a 10% solution of tetraethylammonium hydroxide with perchloric acid. Filtration gave tetraethylammonium perchlorate which was recrystallized from water and dried under vacuum over phosphorus pentoxide.

The acetonitrile used was Matheson Coleman & Bell spectroquality reagent.

Kinetic Methods.—All runs were carried out in stoppered volumetric flasks. Aliquots of 4.93 ml., taken with an insulated pipet, were delivered into 30 ml. of acetone previously cooled into solid carbon dioxide–acetone slush.

Measurement of the Extent of Acid Formation.—Analysis was by titration in 30 ml. of acetone, previously rendered neutral to the lacmoid indicator against a standard solution of sodium methylate in methanol.

Measurement of the Extent of Bromide Ion Production.—Analysis was by potentiometric titration against standard aqueous 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 dip-type calomel reference electrode were used.

Product Studies.[5]—A 100-ml. solution, 0.0227 *M* in bromotetralone I and 0.0433 *M* in tetraethylammonium chloride, was allowed to react for 24 hr. at 37.0°. Two 5-ml. aliquots were removed and both indicated 100% olefin formation as determined by titration of the acid developed. The remaining solution was evaporated to dryness and the solid well washed with water. After drying 530 mg. (99% yield calculated as unsaturated ketone) of a white solid was obtained, m.p. 111–112°, the endocyclic unsaturated ketone II.[4] The mixed m.p. with an authentic sample of the unsaturated ketone II was 110–112°. The infrared and ultraviolet spectra of the product were superimposable upon those obtained for authentic samples of the endocyclic unsaturated ketone II.

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[4] A. Hassner and N. H. Cromwell, *J. Am. Chem. Soc.*, **80**, 893 (1958).

[5] Melting points were read with a calibrated thermometer. Ultraviolet absorption spectra were determined with a Cary Model 11-MS recording spectrophotometer using reagent grade methanol solutions. Infrared spectra were measured with a Perkin-Elmer Model 21 double beam recording instrument employing sodium chloride optics and matched sodium chloride cells with carbon tetrachloride solutions.

Nucleosides. II. 5′-O-Mesylthymidine and 3′-O-Mesylthymidine[1]

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A related study required an expedient synthetic route to the title compounds. The synthesis of 5′-O-mesylthymidine (If) was modeled after the 5′-O-tosyl analog[2] which proceeds from thymidine (Ia) by a series of reactions consisting, in the main, of alternate blocking and deblocking of both alcohol functions in Ia. The successive conversion of Ia first to 5′-O-tritylthymidine (Ib), the acetylation of Ib to form 3′-O-acetyl-5′-O-tritylthymidine (Ic), and detritylation of Ic to give 3′-O-acetylthymidine (Id) constitute three key transformations in the sequence.

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[2] A. M. Michelson and A. R. Todd, *J. Chem. Soc.*, 816 (1955).