

the extract was colored blue. An infrared curve of the blue crystalline compound was in all respects identical to a spectrum of compound B.

Method B.—2-Keto-4,5,6,7-dibenzocoumaran (51 mg.) and selenium dioxide (28 mg.) were refluxed with acetic anhydride (3 ml.) for 4 hours. The solution quickly turned

blue. The acetic anhydride was partially removed at the water aspirator and 50 mg. (100%) of a dark crystalline solid obtained. The infrared spectrum of the compound was identical in all respects with the spectrum of an authentic sample of compound B. The condensation, when run in ethanol, also led to compound B in smaller yield.

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Elimination Reactions of α -Halogenated Ketones. V.¹ Kinetics of the Bromide Ion Promoted Elimination Reaction of 2-Benzyl-2-bromo-4,4-dimethyl-1-tetralone in Solvent Acetonitrile

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2-Benzyl-2-bromo-4,4-dimethyl-1-tetralone (I) has been found to undergo a facile bromide ion-promoted elimination in solvent acetonitrile to yield only the endocyclic α,β -unsaturated ketone, 2-benzyl-4,4-dimethyl-1-keto-1,4-dihydronaphthalene (II). Comparison of the kinetic order in salt, reaction rate and variation of reaction rate with temperature for tetraethylammonium bromide and for piperidine hydrobromide, used as the source of bromide ions, shows that only sufficiently dissociated bromide ions are capable of promoting the elimination reaction.

It has been shown in previous publications² that under a wide variety of conditions dehydrobromination of 2-benzyl-2-bromo-4,4-dimethyl-1-tetralone (I) produces mainly, if not exclusively, the endocyclic unsaturated ketone, 2-benzyl-4,4-dimethyl-1-keto-1,4-dihydronaphthalene (II). This article reports such an elimination reaction promoted in acetonitrile solution by bromide ions when supplied either as tetraethylammonium bromide or as piperidine hydrobromide. The system is a convenient one to study since any concurrent substitution reaction will regenerate the bromotetralone I.

The elimination reaction promoted by the tetraethylammonium bromide was found to be kinetically first order in both bromotetralone I and in tetraethylammonium bromide. At 90.3°, reaction was capable of proceeding to at least 93% decomposition of the bromotetralone I, as measured by acid formation. From the temperature variation of the second-order coefficient, values for the frequency factor of $10^{10.9}$ and for the activation energy of 19.7 kcal./mole were obtained. Product studies lead to the isolation of a good yield of the endocyclic unsaturated ketone II.

The elimination reaction promoted by piperidine hydrobromide was found to be kinetically first order in bromotetralone I, but only an half integral order in piperidine hydrobromide was found. At 90.3°, reaction was capable of proceeding to at least 88% decomposition of the bromotetralone I as measured by acid formation. The temperature variation of the 3/2 order rate coefficient leads to values for the Arrhenius parameter A of $10^{9.5}$ and of the Arrhenius parameter E of 20.2 kcal./mole.

The actual reaction rates were in all cases considerably lower for a given concentration of piperidine hydrobromide than for an identical concentration of tetraethylammonium bromide; e.g., for a salt concentration of 0.0200 M the rate is lower by a factor of about seven.

It appears that only sufficiently dissociated bromide ions are capable of promoting elimination reaction with the bromotetralone I. In this way the lower reaction rates and kinetic order in piperidine hydrobromide relative to tetraethylammonium bromide can be explained on the assumption that virtually all bromide ions in tetraethylammonium bromide are sufficiently dissociated but in piperidine hydrobromide only a small proportion of the bromide ions are in such a state. Conductivity measurements support this view of the mechanism since it has been shown that quaternary substituted ammonium salts are far more dissociated in acetonitrile solution than only partially substituted ammonium salts.³

The value for the Arrhenius parameter, E , for elimination reaction promoted by piperidine hydrobromide, 20.2 kcal./mole, is only slightly higher than the value for the activation energy for bromide ion promoted elimination as obtained from elimination promoted by tetraethylammonium bromide, 19.7 kcal./mole. This is consistent with the proposed view that the reaction mechanism is essentially identical for attack by both bromide salts. The Arrhenius parameter E , of 20.2 kcal./mole, will be a composite constant of the activation energy, 19.7 kcal./mole, together with a smaller contribution governed by the rate of increase in the degree of dissociation of the piperidine hydrobromide with temperature.

Analysis in terms of the various order rate coefficients throughout was carried out using their initial values since it was found that the integrated values for the first-order rate coefficients, calculated with respect to the bromotetralone I, fell steadily throughout each run for both of the bromide salts employed. It is probable that the hydrogen bromide produced participates in an equilibrium which to some extent removes bromide ions from solution with formation of HBr_2^- triple ions.

Deductions which can be made regarding the mechanism of the reaction are deferred until a

(1) For paper IV in this series see N. H. Cromwell and P. H. Hess, *J. Am. Chem. Soc.*, **83**, 1237 (1961).

(2) (a) A. Hassner and N. H. Cromwell, *ibid.*, **80**, 893 (1958); (b) **80**, 901 (1958); (c) N. H. Cromwell, R. P. Ayer and P. W. Foster, *ibid.*, **82**, 130 (1960).

(3) P. Walden and E. J. Birr, *Z. physik. Chem.*, **144A**, 269 (1929).

detailed consideration of the mechanism is made in the following paper.

Experimental Results

The concentrations reported in this paper were not corrected for expansion of the solvent from room temperature to reaction temperature. Other entities quoted which are concentration dependent are similarly uncorrected.

Stability of 2-Benzyl-2-bromo-4,4-dimethyl-1-tetralone (I) in Solvent Acetonitrile.—Solutions of I in acetonitrile were found not to have developed any appreciable acidity after several days at room temperature. At 60.0° a slow first-order decomposition as measured by acid formation occurs. A 0.0100 *M* solution gave a value for the first-order coefficient, k_1 , of 3.0×10^{-7} sec.⁻¹ and a 0.0200 *M* solution gave a value of 3.2×10^{-7} sec.⁻¹. For at least the first 25% decomposition no drift in the values for the first-order coefficient is observed.

TABLE I

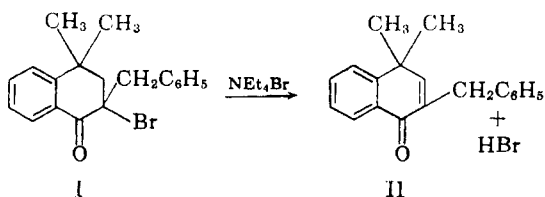
INTEGRATED FIRST-ORDER RATE COEFFICIENTS FOR ACID FORMATION, k_1 (SEC.⁻¹), IN THE DECOMPOSITION OF 0.0200 *M* 2-BENZYL-2-BROMO-4,4-DIMETHYL-1-TETRALONE (I) IN SOLVENT ACETONITRILE AT 60.0°. USING 5.05-ML. ALIQUOTS OF A SOLUTION MADE UP AT 24°

Time, min.	0	890	3880	6880	10,120	14,440
Vol. of 0.0100 <i>M</i> morpholine soln., ml.	0.06	0.25	0.93	1.41	1.99	2.71
$10^7 k_1$..	3.19	3.53	3.10	3.16	3.17

Stability of Bromotetralone I in Solvent Acetonitrile in the Presence of Tetraethylammonium Bromide.—Reaction for 94 hours at 60.0° of a 0.0200 *M* solution of bromotetralone I with 0.0200 *M* tetraethylammonium bromide was found to give at least an 81% yield of a product which was mainly the endocyclic unsaturated ketone, 2-benzyl-4,4-dimethyl-1-keto-1,4-dihydronaphthalene (II), but with a little unchanged bromotetralone I contained.

Titration of acid developed indicated that at 90.3° the decomposition of a solution 0.0100 *M* in bromotetralone I in the presence of 0.0200 *M* tetraethylammonium bromide proceeds to at least 93% completion.

The extent of elimination reaction was in each case determined by titration of the acid developed; but for a run at 60.0° with bromotetralone I 0.0200 *M* and tetraethylammonium bromide 0.00955 *M* the extent of reaction was also determined by potentiometric titration of the bromide ion developed. The extent of reaction at any given time was found to be independent of whether it was determined in terms of hydrogen ion production or in terms of bromide ion production. This is consistent with the proposed reaction scheme



During the initial stages of reaction, at each of the three temperatures for which the reaction rates were measured, second-order kinetics, first order in both bromotetralone I and in tetraethylammonium bromide, were observed within the concentration range studied, 0.00250 *M* to 0.0200 *M* in either reactant.

Since the concentration of tetraethylammonium bromide remains constant, if no interference by the hydrogen bromide produced occurs, the kinetics throughout each run should be pseudo-first order. Hydrogen bromide would not be expected to promote elimination to any marked degree since no autocatalysis was observed during the elimination reaction in the absence of added salt. It was indeed found that as reaction proceeds a steady fall off in the value for the second-order coefficient was observed throughout each individual run.

TABLE II

INITIAL SECOND-ORDER RATE COEFFICIENTS, k_2 (LITERS MOLES⁻¹ SEC.⁻¹), FOR ACID PRODUCTION IN THE REACTION OF 2-BENZYL-2-BROMO-4,4-DIMETHYL-1-TETRALONE WITH TETRAETHYLAMMONIUM BROMIDE IN ACETONITRILE AT VARIOUS TEMPERATURES

<i>t</i> , °C.	[Bromotetralone]	[NEt ₄ Br]	$10^4 k_2$
29.6	0.0100	0.00478	0.40
29.6	.0200	.00955	0.44
60.0	.0100	.00250	8.5
60.0	.0100	.00478	8.0
60.0	.00500	.00955	8.8
60.0	.0100	.00955	8.7
60.0	.0200	.00955	9.1 ^a
60.0	.0100	.0200	8.9
75.0	.0100	.00250	30.8
75.0	.0100	.00955	32.3

^a Initial second-order rate coefficient for bromide ion production: 8.9×10^{-3} l. moles⁻¹ sec.⁻¹.

An Arrhenius plot of the initial values for the second-order rate coefficient leads to a good linear plot and to values for the frequency factor of $10^{10.9}$ and for the activation energy of 19.7 kcal./mole.

Stability of Bromotetralone I in Solvent Acetonitrile in the Presence of Piperidine Hydrobromide.—Reaction for 13 days at 60.0° of a solution 0.0200 *M* in bromotetralone I and 0.00500 *M* in piperidine hydrobromide gave at least a 77% yield, calculated as unsaturated ketone, of a product which was mainly the endocyclic unsaturated ketone II but which contained a little unchanged bromotetralone I.

Measurement of acid developed after 24 hours at 90.3° of a solution 0.0100 *M* in bromotetralone I and 0.00500 *M* in piperidine hydrobromide indicated that decomposition had proceeded to 88% completion. After a further 24 hours, acid present corresponded to only 82% decomposition. Similarly a solution 0.0100 *M* in bromotetralone I and 0.00250 *M* in piperidine hydrobromide gave values corresponding to 85% decomposition after 25 hours and 76% decomposition after 92 hours, with development of a brown coloration within the solution. It appears that a slow side reaction is removing acid from solution and the maximum value for acid production observed will be somewhat lower than the true extent of decomposition.

It was found that values for the integrated first-order coefficient with respect to bromotetralone I fell throughout each individual run rather more markedly than for the tetraethylammonium salt and further the initial values were lower than for when an identical concentration of the tetraethylammonium bromide was used. The initial values for the second-order coefficient were found to fall in value as the concentration of piperidine hydrobromide rose and an analysis in terms of initial 3/2 order rate coefficients was found to lead to constant values for this coefficient as defined by

$$\text{initial velocity} = k_{1/2} [\text{bromotetralone}] [\text{piperidine hydrobromide}]^{1/2}$$

An Arrhenius plot of the initial values for the 3/2 order rate coefficient leads to a good linear plot. Values for the Arrhenius parameter obtained are: for A , $10^9.5$, and for E , 20.2 kcal./mole. Owing to the complex kinetics the Arrhenius parameters cannot be interpreted directly in terms of activation energy and frequency factor; the parameters are composite constants of the above together with other constants governing the dissociation of the piperidine hydrobromide.

TABLE III

INITIAL SECOND-ORDER RATE COEFFICIENTS, k_2 (LITERS MOLES⁻¹ SEC.⁻¹), AND INITIAL 3/2 ORDER RATE COEFFICIENTS, $k_{1/2}$ (LITERS^{1/2} MOLES^{-1/2} SEC.⁻¹), FOR ACID PRODUCTION IN THE REACTION OF 2-BENZYL-2-BROMO-4,4-DIMETHYL-1-TETRALONE (I) WITH PIPERIDINE HYDROBROMIDE IN ACETONITRILE AT VARIOUS TEMPERATURES

t , °C.	[Bromotetralone]	[C ₈ H ₁₁ NHBr]	$10^3 k_2$	$10^4 k_{1/2}$
60.0	0.0100	0.00250	3.44	1.72
60.0	.00500	.00500	2.64	1.87
60.0	.0100	.00500	2.20	1.56
60.0	.0200	.00500	2.40	1.70
60.0	.0100	.0100	1.78	1.78
60.0	.0100	.0200	1.28	1.80
60.0	.0100	.0400	0.76	1.52
75.0	.00500	.00500	8.6	6.1
75.0	.0100	.0200	4.8	6.8
90.3	.0100	.00250	43.6	19.9
90.3	.0100	.00500	28.2	21.8
90.3	.0100	.0200	15.9	22.4

Experimental Methods

Materials.—Preparation of the 2-benzyl-2-bromo-4,4-dimethyl-1-tetralone has been described previously.^{2a} Tetraethylammonium bromide was prepared by neutralizing an aqueous solution of tetraethylammonium hydroxide with hydrobromic acid, evaporating to dryness and recrystallizing from acetonitrile. Piperidine hydrobromide was similarly prepared from hydrobromic acid and piperidine. The acetonitrile was Matheson, Coleman and Bell spectro-quality reagent.

Kinetic Methods.—All runs were carried out by means of the sealed bulb technique. The sealed bulbs were prepared from 16 × 150 mm. test-tubes and each aliquot of reaction mixture was of 5.05 ml. at room temperature. As each sealed bulb was removed from the thermostat, reaction was quenched by immersion in solid CO₂-alcohol slush until analyzed.

Measurement of the Extent of Acid Formation.—Analysis was by titration in 20 ml. of acetone, previously rendered neutral to the Lacmoid indicator, against a standard solution of morpholine in methanol. The morpholine solution was accurately prepared by direct weighing of the morpholine and checked by titration against standard hydrochloric acid solution.

The analyses of a few runs illustrating the method used to obtain initial values for the rate coefficients from the determination at various time intervals of the extent of olefin formation by acidity measurements are given below. In each instance the integrated values for first-order rate coefficient, k_1 (sec.⁻¹), are calculated with respect to the bromotetralone I. In each case an initial value for k_1 is obtained by extrapolation to zero extent of reaction of a plot of k_1 against extent of reaction, expressed in ml. of standard hydrogen bromide produced, as determined by titration of hydrogen ion.

(A) Temperature: 90.3°; 5.05-ml. aliquots at 24°; [bromotetralone]: 0.0100 M ; [C₈H₁₁NHBr]: 0.0200 M ; titers are in ml. of 0.0118 M morpholine solution

Time, min.	0	4	8	12	17	24	32
Titer	0.23	0.51	0.75	0.98	1.17	1.41	1.65
$10^4 k_1$..	29.9	28.6	28.4	25.9	23.9	22.5

Initial k_1 is 31.8×10^{-3} sec.⁻¹, corresponding to an initial second order coefficient of 15.9×10^{-3} l. moles⁻¹ sec.⁻¹.

(B) Temperature: 60.0°; 5.05-ml. aliquots at 24°; [bromotetralone]: 0.0200 M ; [C₈H₁₁NHBr]: 0.00500 M ; titers are in ml. of 0.0116 M morpholine solution

Time, min.	0	32	60	90	124
Titer	0.06	0.27	0.41	0.58	0.74
$10^4 k_1$..	1.28	1.15	1.15	1.10
Time, min.	180	244	280	1180	1480
Titer	0.96	1.16	1.30	2.91	3.26
$10^4 k_1$	1.02	0.93	0.92	0.56	0.52

Initial k_1 is 1.20×10^{-3} sec.⁻¹, corresponding to an initial second order coefficient of 2.40×10^{-3} l. moles⁻¹ sec.⁻¹.

(C) Temperature: 60.0°; 5.05-ml. aliquots at 24°; [bromotetralone]: 0.0100 M ; [NEt₄Br]: 0.00250 M ; titers are in ml. of 0.0116 M morpholine solution

Time, min.	0	30	60	90	120	180	250
Titer	0.11	0.26	0.40	0.51	0.62	0.76	0.96
$10^4 k_1$..	2.00	1.96	1.83	1.77	1.54	1.49

Initial k_1 is 2.12×10^{-3} sec.⁻¹, corresponding to an initial second order coefficient of 8.5×10^{-3} l. moles⁻¹ sec.⁻¹.

(D) Temperature: 60.0°; 5.05-ml. aliquots at 24°; [bromotetralone]: 0.0200 M ; [NEt₄Br]: 0.00955 M ; titers are in ml. of 0.0114 M morpholine solution

Time, min.	0	4	8	12	16	20	26	36
Titer	0.21	0.38	0.55	0.70	0.85	0.96	1.13	1.41
$10^4 k_1$..	8.3	8.3	8.1	8.0	7.6	7.2	6.9

Initial k_1 is 8.7×10^{-3} sec.⁻¹, corresponding to an initial second order coefficient of 9.1×10^{-3} l. moles⁻¹ sec.⁻¹.

Measurement of the Extent of Bromide Ion Production.—One run was followed by determination of the rate of formation of bromide ions. The concentrations and temperature were identical with the illustrative run (D) given for measurement of rate of acid formation.

Analysis was by means of 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. (A) **Elimination Promoted by Tetraethylammonium Bromide.**—Sixty ml. of a solution 0.0200 M in both bromotetralone I and in tetraethylammonium bromide was allowed to react for 94 hours at 60.0°. The solution was evaporated to dryness and after ether extraction the filtrate was evaporated to dryness; 0.254 g. of a product,

(4) Melting points were read with a calibrated thermometer. Ultra-violet 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.

Temperature: 60.0°; 5.05-ml. aliquots at 24°; [bromotetralone]: 0.0200 *M*; [NEt₃Br]: 0.00955 *M*; titers are in ml. of 0.0100 *M* silver nitrate; the initial [NEt₃Br] is equivalent to a titer of 4.82 ml.; the integrated first-order rate coefficients, k_1 (sec.⁻¹), are calculated with respect to the bromotetralone I

Time, min.	0	8	20	40	60	90	180
Titer	5.16	5.50	6.01	6.65	7.12	7.72	8.61
10 ⁵ k_1	..	7.3	7.6	6.9	6.2	5.6	4.0

By extrapolation to zero reaction of a plot of k_1 against the extent of reaction, expressed in ml. of 0.0100 *M* Br⁻ produced, an initial value for k_1 of 8.5×10^{-3} sec.⁻¹ is obtained, corresponding to an initial second-order coefficient of 8.9×10^{-3} l. moles⁻¹ sec.⁻¹

an 81% yield calculated as unsaturated ketone, was obtained. A solution in acetonitrile of a portion of the product gave a slight precipitate with silver nitrate indicating the presence of a trace of unreacted bromotetralone I.³⁰ The melting point of the crude product was 105–109°. After recrystallization of a portion from methanol the melting point 113–114° corresponded to that for pure endocyclic unsaturated ketone II^{2a}; the recrystallized product gave no precipitate with an acetonitrile solution of silver nitrate.

The infrared spectrum of the crude product had $\nu_{C=O}$ 1662/95, corresponding to the endocyclic unsaturated

ketone II.^{2a} No disturbance was observed at 1673 cm.⁻¹, where the exocyclic unsaturated ketone III would give a peak.^{2a} A small shoulder was observed at $\nu_{C=O}$ 1687/38, where the reactant bromotetralone I shows a peak.^{2a} The recrystallized material had $\nu_{C=O}$ 1663/96 and no shoulder at 1687 cm.⁻¹, where the absorption was 28%. The ultraviolet spectrum of the crude product had the form predicted for endocyclic unsaturated ketone II^{2a}; λ_{max} 254 m μ (ϵ 14,800); λ_{min} 228 m μ (ϵ 8,200).

The ultraviolet spectra of II and III are quite different in character^{2a} and in particular in the region 320–340 m μ III absorbs strongly while II has virtually no absorption. Absorption in this region was found to be extremely low.

(B) Elimination Promoted by Piperidine Hydrobromide.—Twenty-five ml. of a solution initially 0.0200 *M* in bromotetralone I and 0.00500 *M* in piperidine hydrobromide was left for 13 days at 60.0° and the solution then evaporated to dryness. After ether extraction the filtrate was evaporated to dryness. A 0.10-g. amount of brownish residue was isolated. The yield calculated as unsaturated ketone was 77%. The infrared spectrum of the crude material had $\nu_{C=O}$ 1663/92 and a shoulder 1686/41 with no disturbance at 1673 cm.⁻¹. The product was endocyclic unsaturated ketone II with a little unreacted bromotetralone I.^{2a} On recrystallization from methanol a white solid, m.p. 111–112°, was obtained which was endocyclic unsaturated ketone II.^{2a}

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[CONTRIBUTION FROM AVERY LABORATORY, UNIVERSITY OF NEBRASKA, LINCOLN 8, NEBR.]

Elimination Reactions of α -Halogenated Ketones. VI.¹ Kinetics of Piperidine Promoted Elimination from 2-Benzyl-2-bromo-4,4-dimethyl-1-tetralone in Solvent Acetonitrile

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2-Benzyl-2-bromo-4,4-dimethyl-1-tetralone (I) has been found to undergo a facile piperidine-promoted elimination in solvent acetonitrile to yield mainly the endocyclic α,β -unsaturated ketone, 2-benzyl-4,4-dimethyl-1-keto-1,4-dihydronaphthalene (II) together with a smaller amount of the exocyclic α,β -unsaturated ketone 2-benzal-4,4-dimethyl-1-tetralone (III). The reaction was found to be kinetically first order in the bromotetralone I and of both a zero order and a first order component in piperidine. A merged substitution and elimination mechanism for the dehydrobromination reactions of bromotetralone I is proposed.

Introduction.—It has been shown in a previous publication^{2b} that dehydrobromination of 2-benzyl-2-bromo-4,4-dimethyl-1-tetralone (I) with amines leads to mainly the endocyclic α,β -unsaturated ketone, 2-benzyl-4,4-dimethyl-1-keto-1,4-dihydronaphthalene (II) together with some of the exocyclic α,β -unsaturated ketone, 2-benzal-4,4-dimethyl-1-tetralone (III).

Discussion of Results

This investigation shows that the actual composition ratios in the product must be treated with reservation as regards representation of the way in which the piperidine-promoted elimination reaction divides between the two unsaturated ketones. As reaction proceeds a bromide ion-promoted elimination reaction becomes of increasing importance and this reaction has been shown¹ to produce only the endocyclic unsaturated ketone II. In this in-

vestigation an acetonitrile solution 0.0200 *M* in bromotetralone I and 0.0400 *M* in piperidine after reacting to completion at 60.0° gave 87% of II and 13% of III. The figure of 13% must, however, be regarded as only a minimum figure for the percentage of *exo*-elimination in the piperidine promoted reaction.

The elimination reaction promoted by piperidine was found to be kinetically first order in bromotetralone I but of indefinite order in piperidine. The order in piperidine was found to consist of two components, one of zero order and one of first order. The velocity of the piperidine promoted elimination reaction (v) could be expressed

$$v = [\text{bromotetralone}](k_1^0 + k_2^0[\text{piperidine}])$$

where k_1^0 and k_2^0 are the first- and second-order rate coefficients for the piperidine promoted elimination. During each individual run the kinetics were complicated by an autocatalysis due to the formation of piperidine hydrobromide.¹ To avoid consideration of this intervention, the kinetic data were analyzed in terms of initial values for the rate coefficients.

(1) For paper V in this series see D. N. Kevill and N. H. Cromwell, *J. Am. Chem. Soc.*, **83**, 3812 (1961).

(2) (a) A. Hassner and N. H. Cromwell, *ibid.*, **80**, 893 (1958); (b) **80**, 901 (1958); (c) N. H. Cromwell, R. P. Ayer and P. W. Foster, *ibid.*, **82**, 130 (1960).