

min., during which 48.0 ml. (23°, 744.2 mm.) had been absorbed. The catalyst was removed by suction filtration at about -80°. Vapor chromatography of a sample of the filtrate on the analytical column revealed in addition to solvent two peaks of relative area 77:23. These volatile products were transferred *in vacuo* at room temperature into a liquid nitrogen trap to separate them from the high-boiling diglyme. The mixture was once again subjected to g.l.c. and the two peaks were trapped separately. Comparison of the g.l.c. retention time and infrared spectrum with those of an authentic sample identified the larger peak as methylcyclopentane. Identity with authentic material in terms of retention times and n.m.r. spectra established that the peak of smaller area was bicyclo[2.1.1]hexane (7). The hydrogen uptake required to produce a 77:23 mixture of methylcyclopentane and 7 is calculated to be 1.77 equivalents; the observed 48.0 ml. uptake corresponds to 1.73 equivalents, or about 2% less than the theoretical.

Another hydrogenation experiment using the same solvent and catalyst was arbitrarily interrupted after only about 0.9 equivalent of hydrogen had been absorbed. A vapor phase chromatogram of the volatile products displayed peaks (in order of increasing retention time) corresponding to methylcyclopentane, bicyclo[2.1.1]hexane, unidentified product, and starting material. Relative areas were 25:13:24:38. Further hydrogenation of this mixture resulted in the disappearance of the unidentified peak as well as starting material, and again only methylcyclopentane and 7 remained. The unknown substance was tentatively identified as 1-methylcyclopentene by its n.m.r. spectrum. An authentic, chromatographically homogeneous sample of this compound

was prepared by dehydration with 85% phosphoric acid of 1-methylcyclopentanol. Comparison (retention times; infrared, n.m.r. spectra) with the unknown confirmed the structure assignment. It is important to note that the n.m.r. spectrum of the crude hydrogenation product had revealed the presence of 1-methylcyclopentene, thus ruling out the possibility that the olefin was an artifact arising from g.l.c.

Six per cent palladium-strontium carbonate was substituted for the 10% palladium-charcoal used in the preceding hydrogenation experiment in order to eliminate acid catalysis as an explanation for olefin formation. The product distribution corresponded closely with that observed using charcoal as the support. When a diglyme solution of 1 was stirred with 10% palladium-charcoal for many hours in the absence of hydrogen, the tricyclic compound remained unchanged as indicated by g.l.c.

The bicyclic hydrocarbon 5 failed to absorb hydrogen at atmospheric pressure over 10% palladium-charcoal in diglyme solution. Vapor chromatography of the product revealed only starting material.

Acknowledgment.—We wish to thank Dr. Earl Lumpkin of the Humble Oil Co. for measuring the mass spectra and Dr. Kenneth Kirk for a loan of photolysis apparatus and for a sample of bicyclo[2.2.0]hexane. We are grateful to the donors of the Petroleum Research Fund of the American Chemical Society and to the National Science Foundation for generous financial support.

[CONTRIBUTION FROM THE AVERY LABORATORY, UNIVERSITY OF NEBRASKA, LINCOLN, NEB.]

Elimination Reactions of α -Halogenated Ketones. XII.^{1a} Carbon-Halogen and Carbon-Hydrogen Bond Strengths as Orientation and Rate-Determining Factors. Deuterium Isotope Effects in Dehydrobromination of 2-Bromo-2-benzyl-1-indanone^{1b}

BY DENNIS N. KEVILL, GUILLAUME A. COPPENS, AND NORMAN H. CROMWELL^{1c}

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It has been found that, in halide ion promoted elimination from α -halogenated tetralones and indanones, the strength of the carbon-halogen bond is an extremely important rate-determining factor. Deuterium substitution for the *exo*-benzylic methylene protons of 2-bromo-2-benzyl-1-indanone (IV) leads to a low deuterium isotope effect, consistent with the transition state of the rate-determining step having carbon-halogen bond breaking running well ahead of carbon-hydrogen bond breaking. Attack of piperidine upon 2-bromo-2-(α,α -dideuteriobenzyl)-1-indanone (IVa) leads to substantial yields of 3-piperidino-2-(α,α -dideuteriobenzyl)-1-indanone (VIa) formed by an endocyclic dehydrobromination followed by a 1,4-addition. The exocyclic deuterium substitution leads to a marked change in the reaction pathway and suggests the possible use of deuterium substitution for controlling the orientation of elimination in other delicately balanced systems.

Previous communications within this series have reported upon the kinetics of elimination reactions of several α -halogenated tetralones¹⁻⁶ and of 4-biphenyl-1-bromocyclohexyl ketone.⁷ These reactions were discussed in terms of a mechanism of merged substitution and elimination.^{3,8}

More recently it was proposed elsewhere⁹ that bimolecular dehydrohalogenation from tertiary halide

structures proceeds by a mechanism similar to the classical E2 mechanism but with the reaction passing through a transition state in which a considerable amount of E1 character is incorporated. These two mechanisms differ only subtly in character.⁶ Both incorporate considerable carbon-halogen bond breaking in the transition state accompanied by only a weakly developed rupture of the carbon-hydrogen bond. This present communication reports upon studies which show that bimolecular dehydrohalogenation of tertiary α -halogenated ketones can proceed *via* a transition state which incorporates both of these features.

Discussion of Results

Halide ion promoted elimination from 2-benzyl-2-halogeno-4,4-dimethyl-1-tetralone in acetonitrile was found to lead exclusively to the thermodynamically

than halide leaving groups have caused some amplification of the views expressed in ref. 9a: J. F. Bunnett and E. Baciocchi, *Proc. Chem. Soc.*, 238 (1963). It is interesting to observe that these trends are fully consistent with, and can be predicted from, the mechanism of merged substitution and elimination.^{3,4}

(1) (a) For paper XI in this series see D. N. Kevill, P. W. Foster, and N. H. Cromwell, *J. Org. Chem.*, **28**, 1476 (1963). (b) Presented in part at the XIXth International Congress of Pure and Applied Chemistry, London, July 10-17, 1963. (c) To whom communications concerning this article should be addressed.

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

(3) D. N. Kevill and N. H. Cromwell, *ibid.*, **83**, 3815 (1961).

(4) G. A. Coppens, D. N. Kevill, and N. H. Cromwell, *J. Org. Chem.*, **27**, 3299 (1962).

(5) D. N. Kevill, G. A. Coppens, and N. H. Cromwell, *ibid.*, **28**, 567 (1963).

(6) D. N. Kevill and N. H. Cromwell, *Tetrahedron Letters*, **4**, 255 (1963).

(7) D. N. Kevill, P. H. Hess, P. W. Foster, and N. H. Cromwell, *J. Am. Chem. Soc.*, **84**, 983 (1962).

(8) D. N. Kevill and N. H. Cromwell, *Proc. Chem. Soc.*, 252 (1961).

(9) (a) J. F. Bunnett, G. T. Davis, and H. Tanida, *J. Am. Chem. Soc.*, **84**, 1606 (1962). (b) Trends observed on extending measurements to other

more stable Saytzeff product¹⁰ 2-benzyl-4,4-dimethyl-1-keto-1,4-dihydronaphthalene (I). In promoting elimination from either 2-benzyl-2-bromo-4,4-dimethyl-1-tetralone (II) or 2-benzyl-2-chloro-4,4-dimethyl-1-tetralone (III) the chloride ion was, at 25°, about 20 times as effective as the bromide ion. At 25°, bromotetralone II reacted faster than chlorotetralone III by a factor of 1500 in chloride ion-promoted elimination and faster by a factor of 1160 in bromide ion-promoted elimination.

TABLE I

THE ARRHENIUS PARAMETERS AND CALCULATED SECOND-ORDER RATE COEFFICIENTS AT 25.0°, k_2^{25} , FOR DEHYDROHALOGENATION OF 2-BENZYL-2-HALOGENO-4,4-DIMETHYL-1-TETRALONE AS PROMOTED BY CHLORIDE IONS AND BY BROMIDE IONS IN ACETONITRILE, $k_2 = Ae^{-E/RT}$ L. MOLE⁻¹ SEC.⁻¹

Reactants	E, kcal./mole	log ₁₀ A	10 ⁴ k_2^{25} , l. mole ⁻¹ sec. ⁻¹
Bromotetralone II + NEt ₄ Br ³	19.7	10.9	2900
Bromotetralone II + NEt ₄ Cl ⁴	18.5	11.4	69000
Chlorotetralone III + NEt ₄ Br	25.5	12.1	2.5
Chlorotetralone III + NEt ₄ Cl ⁵	24.6	12.7	46

The factor of prime importance in determining the rates of elimination is the ease of rupture of the carbon-halogen bond, which is determined by the identity of the covalently bound halogen. The identity of the attacking halide ion involved in the bimolecular process is of only secondary importance.

A deuterated analog of 2-bromo-2-benzyl-1-indanone (IV) was prepared by condensing 1-indanone with deuteriobenzaldehyde (C₆H₅CD₀), deuterating the resultant α,β -unsaturated ketone, and then brominating in the α -position to give 2-bromo-2-(α,α -dideuteriobenzyl)-1-indanone (IVa).

Dehydrobromination of IV or IVa by use of bromide ions in acetonitrile proceeds with formation of the corresponding 2-benzal-1-indanone (V) or 2-(α -deuteriobenzal)-1-indanone (Va). The proton magnetic resonance spectrum of Va formed in this way contains a sharp singlet, due to the 3-position methylene protons, at 5.97 τ . The singlet corresponds in intensity to two protons and it follows that no appreciable amount of reaction can proceed by an endocyclic dehydrobromination followed by intramolecular rearrangement to Va. Such a rearrangement would lead to deuterium in the 3-position and a reduced signal intensity. The kinetics of the reaction were investigated at several temperatures and with varying reactant concentrations and found to be of first order in IV or IVa and of first order in bromide ion. Mean values for the initial second-order rate coefficients are reported in Table II; values fall slightly throughout a run due to removal of bromide ions as HBr₂⁻ ions.²

The deuterium isotope effects (k_2^H/k_2^D) were of the same order of magnitude as those previously observed^{9a} for anionic promoted elimination reactions of tertiary halides in ethanol. Our system is more amenable to analysis in that only the derived dehydrohalogenation product was formed and further it was initially formed with clean second-order kinetics.

(10) The corresponding exocyclic isomer was rearranged to I by boiling with palladium on charcoal in ethylene glycol: N. H. Cromwell, R. P. Ayer, and P. W. Foster, *J. Am. Chem. Soc.*, **82**, 130 (1960). It was, however, stable in acetonitrile solutions of piperidine or tetraethylammonium bromide: D. N. Kevill, E. Weiler, and N. H. Cromwell, unpublished results.

TABLE II

MEAN VALUES FOR THE INITIAL SECOND-ORDER RATE COEFFICIENTS FOR ACID OR FOR BROMIDE ION PRODUCTION IN THE REACTION OF 2-BROMO-2-BENZYL-1-INDANONE (IV), k_2^H , AND OF 2-BROMO-2-(α,α -DIDEUTERIOBENZYL)-1-INDANONE (IVa), k_2^D , WITH TETRAETHYLAMMONIUM BROMIDE IN ACETONITRILE

t, °C.	10 ⁴ k_2^H , l. mole ⁻¹ sec. ⁻¹	10 ⁴ k_2^D , l. mole ⁻¹ sec. ⁻¹	k_2^H/k_2^D
59.8	1.45 ± 0.01	0.43 ± 0.02 ^a	3.4 ± 0.2
60.8		0.48 ± .02	
74.0		1.9 ± .1	
74.8	6.7 ± 0.1	2.05 ± .1 ^a	3.3 ± 0.2
89.8	26.6 ± 0.3	9.4 ± .4	2.8 ± .2
100.8	75 ± 4	24.2 ± .8	3.0 ± .2

^a Value adjusted from one at closely related temperature by means of the Arrhenius parameters: $k_2^H = Ae^{-E/RT}$, $A = 10^{11.5}$ l. mole⁻¹ sec.⁻¹, $E = 23.3$ kcal./mole; $k_2^D = Ae^{-E/RT}$, $A = 10^{11}$ l. mole⁻¹ sec.⁻¹, $E = 24.3$ kcal./mole.

Complications due to reaction with solvent, accompanying substitution, and formation of other dehydrohalogenation products were avoided. A relatively small value for the deuterium isotope effect can mean either that C-H (C-D) bond breaking has proceeded little or has proceeded far in the transition state. We interpret our kinetic results in the same way as Bunnett, Davis, and Tanida^{9a}; *i.e.*, we believe they indicate that the extent of rupture of the carbon-hydrogen bond in the transition state is less than that in the transition state of a fully synchronous E2 reaction. Independent evidence supporting this interpretation has previously been obtained.³

This kinetic isotope effect is fully consistent with the observation in the related tetralone series that the ease of rupture of the carbon-halogen bond is an extremely important rate-determining factor. These two substituent effects are consistent with any picture proposed for these reactions in which carbon-halogen bond rupture is, in the transition rate, running well ahead of carbon-hydrogen bond rupture.

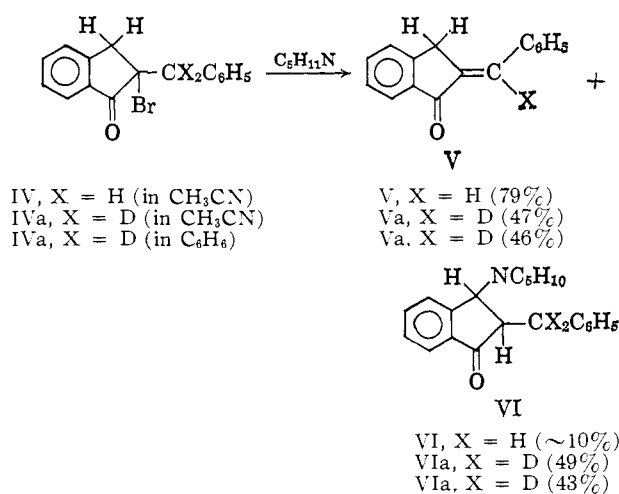
Although bromide ion promoted elimination from IV or IVa led exclusively to the exocyclic isomer, it is possible that other reagents may in part proceed *via* an initial endocyclic elimination to give the unstable 2-benzyl-1-indone. Several reactions of 2-bromo-2-(α -bromobenzyl)-1-indanone were found to proceed *via* an initial endocyclic dehydrobromination,¹¹ and it is also known that α -bromotetralone II, in its reactions with amines in benzene, gives appreciable yields of the thermodynamically unstable exocyclic α,β -unsaturated tetralone.^{1a} It was therefore not too surprising that reaction of α -bromoindanone IV with piperidine in acetonitrile led, as indicated by the proton magnetic resonance spectrum, to a 79% yield of 2-benzal-1-indanone (V) and to approximately 10% of a product identified as 3-piperidino-2-benzyl-1-indanone (VI). The product VI was formed by an endocyclic dehydrobromination followed by a 1,4-addition of piperidine to the unstable 2-benzyl-1-indone.

When the reaction was repeated using the deuterated analog IVa, the rate of competing exocyclic elimination was reduced and there was a corresponding increase in the percentage yield of the piperidino derivative, 3-piperidino-2-(α,α -dideuteriobenzyl)-1-indanone (VIa), as formed by endocyclic elimination-addition. 3-Piperidino-2-(α,α -dideuteriobenzyl)-1-indanone hydra-

(11) B. D. Person, R. P. Ayer, and N. H. Cromwell, *J. Org. Chem.*, **27**, 3038 (1962).

chloride (VIIa) was isolated from the reaction mixture and characterized.

The product ratio between Va and VIa was not significantly altered when the reaction was carried out in benzene rather than in acetonitrile.



In both II and IV there is a delicate balance between endocyclic and exocyclic dehydrobromination. Use of halide ions in acetonitrile, as the elimination promoting reagent, led exclusively to the thermodynamically more stable Saytzeff product. On the other hand, amines were less selective and led to either the Saytzeff or Hofmann product and, in general, gave a mixture of both products.

The reaction of 2-bromo-2-benzyl-1-indanone with piperidine in acetonitrile was found to proceed with clean second-order kinetics; although bromide ions are produced during reaction they react at a sufficiently slow rate relative to piperidine such that no disturbance to the kinetic pattern was observed over at least 80% stoichiometrically possible reaction. The amount of piperidine addition product (~10%) was insufficient for any marked effect upon the kinetic pattern.

Kinetic Results¹²

Stability of Reactants in Acetonitrile.—Piperidine was previously shown to be stable in acetonitrile.⁷ A 0.0100 *M* solution of bromoindanone IV did not develop any appreciable acidity during several days at room temperature; at 90.6° the solution slowly developed acidity. The reaction was found to be subject to a fairly strong autocatalysis.

TABLE III

INTEGRATED FIRST-ORDER RATE COEFFICIENTS, k_1 , FOR ACID PRODUCTION IN THE DECOMPOSITION OF 0.0100 *M* 2-BROMO-2-BENZYL-1-INDANONE IN ACETONITRILE AT 90.6°^a

Time, hr.	0	20	42	66	90	162	258
Reaction, %	0.0	1.1	2.0	4.7	8.2	23.0	33.2
$10^7 k_1$, sec. ⁻¹	...	1.5	1.3	1.6	2.6	4.5	4.3

^a Initial $k_1 = 1.2 \times 10^{-7}$ sec.⁻¹.

Bromide Ion Promoted Elimination from 2-Chloro-2-benzyl-4,4-dimethyl-1-tetralone (III) in Acetonitrile.—

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

The extent of reaction was followed by titration of acid developed. A steady fall-off in values for the integrated first-order rate coefficient with respect to the chlorotetralone III was observed² and initial values were obtained by extrapolation.

TABLE IV

INITIAL VALUES FOR THE SECOND-ORDER RATE COEFFICIENTS FOR ACID PRODUCTION, $k_2^{(H^+)}$, IN THE REACTION OF 2-CHLORO-2-BENZYL-4,4-DIMETHYL-1-TETRALONE (III) WITH TETRAETHYLAMMONIUM BROMIDE IN ACETONITRILE

<i>t</i> , °C.	[Chlorotetralone]	[NEt ₄ Br]	$10^4 k_2^{(H^+)}$, ^a l. mole ⁻¹ sec. ⁻¹
74.0	0.0200	0.0382	1.19
74.0	.0300	.0239	1.17
91.1	.0200	.0382	6.5
91.1	.0200	.0200	6.6
91.1	.0300	.0239	6.5
107.3	.0293	.0389	25.9
107.3	.0198	.0168	26.5

^a $k_2 = Ae^{-E/RT}$, $A = 10^{12.11}$ l. mole⁻¹ sec.⁻¹, $E = 25.5$ kcal./mole.

Bromide Ion Promoted Elimination from 2-Bromo-2-benzyl-1-indanone (IV) and 2-Bromo-2-(α,α -dideuterio-benzyl)-1-indanone (IVa) in Acetonitrile.—Runs were carried out with reactant concentrations in the range 0.01 to 0.04 *M*. A steady fall-off in the values for the first-order coefficient with respect to the bromoindanone was observed throughout each run² and initial values were obtained by extrapolation. Initial values for the second-order rate coefficients have been summarized in Table II.

Piperidine Promoted Elimination from 2-Bromo-2-benzyl-1-indanone in Acetonitrile.—The integrated second-order rate coefficients, first-order in bromoindanone IV and first-order in piperidine, were in each run found to be constant over at least 80% stoichiometrically possible reaction.

TABLE V

MEAN VALUES FOR THE SECOND-ORDER RATE COEFFICIENTS FOR PIPERIDINE NEUTRALIZATION, $k_2^{(H^+)}$, AND FOR THE SECOND-ORDER RATE COEFFICIENTS FOR BROMIDE ION PRODUCTION, $k_2^{(Br^-)}$, IN THE REACTION OF 2-BROMO-2-BENZYL-1-INDANONE (I) WITH PIPERIDINE IN ACETONITRILE

<i>t</i> , °C.	Bromoindanone	Piperidine	$10^3 k_2^{(Br^-)}$, ^a l. mole ⁻¹ sec. ⁻¹	$10^3 k_2^{(H^+)}$, ^a l. mole ⁻¹ sec. ⁻¹
29.9	0.0300	0.0265	1.71	...
29.9	.0400	.0265	1.69	...
29.9	.0300	.0751	...	1.79
41.4	.0200	.0134	3.06	...
41.4	.0100	.0345	3.14	...
41.4	.0200	.0345	3.00	...
61.5	.0200	.0134	9.9	...
61.5	.0300	.0134	...	10.4

^a $k_2 = Ae^{-E/RT}$, $A = 10^{5.1}$ l. mole⁻¹ sec.⁻¹, $E = 11.0$ kcal./mole.

Experimental

Materials.—2-Benzyl-2-bromo-4,4-dimethyl-1-tetralone¹³ (II), 2-benzyl-2-chloro-4,4-dimethyl-1-tetralone³ (III), and 2-bromo-2-benzyl-1-indanone¹⁴ (IV) have previously been prepared.

2-Bromo-2-(α,α -dideuterio-benzyl)-1-indanone (IVa) was prepared by the condensation in the usual manner¹³ of 1-indanone with deuteriobenzaldehyde to give 2-(α -deuteriobenzyl)-1-indanone (Va) which was then quantitatively deuterated, at atmospheric pressure, in carbon tetrachloride containing 10% palladium-on-charcoal as catalyst.¹⁴ The deuterated product was then brominated by the method of Leuchs.¹⁵

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

(14) N. H. Cromwell and R. P. Ayer, *ibid.*, **82**, 133 (1960).

(15) H. Leuchs, J. Wutke, and E. Giesler, *Ber.*, **46**, 2200 (1913).

TABLE VI

(A) Temperature, 41.4°; 4.39-ml. aliquots at 24°; in acetonitrile; [bromindanone IV] = 0.0200 M, [piperidine] = 0.0345 M; potentiometric titration; titers are in ml. of 0.0100 M AgNO₃

Time, min.	0	7.2	17.8	30.7	48.6	70.6	107.6	194.6	255.2	328.6	374.6
Titers	0.06	0.50	1.14	1.75	2.50	3.30	4.35	6.08	6.84	7.80	8.00
10 ³ k ₂	..	2.88	3.15	3.05	3.01	3.07	2.92	2.91	2.80	3.15	2.99

Mean value for k₂ is 3.00 × 10⁻³ l. mole⁻¹ sec.⁻¹

(B) Temperature, 61.5°; 4.93-ml. aliquots at 24°; in acetonitrile; [bromindanone IV] = 0.0300 M, [piperidine] = 0.0134 M; titers are in ml. of 0.0114 M HCl

Time, min.	0	15	30	45	60	75	96	115	135
Titers	5.15	3.93	3.06	2.37	1.90	1.52	1.13	0.90	0.74
10 ³ k ₂	..	10.4	10.5	10.6	10.6	10.6	10.5	10.2	9.6

Mean value for k₂ is 10.4 × 10⁻³ l. mole⁻¹ sec.⁻¹

(C) Temperature, 107.3°; 4.93-ml. aliquots at 24°; in acetonitrile; [chlorotetralone III] = 0.0293 M, [NEt₄Br] = 0.0389 M; titers are in ml. of 0.0114 M NaOMe

Time, min.	0	11	20	28	36	44	58	73	88	117	223
Titers	0.37	1.22	1.88	2.40	2.90	3.34	4.06	4.78	5.41	6.48	9.12
10 ³ k ₂	..	2.56	2.56	2.55	2.52	2.46	2.39	2.36	2.32	2.24	2.06

Initial value for k₂ is 2.59 × 10⁻³ l. mole⁻¹ sec.⁻¹

The purification of piperidine³ and tetraethylammonium bromide² have previously been described. The acetonitrile was Eastman Kodak Co. Spectrograde.

Kinetic Methods.—All runs were carried out using accurately measured aliquots of about 5 ml. in volume. Runs below 60° were carried out by withdrawing samples from a volumetric flask; at and above 60° the sealed bulb technique was employed. The kinetic techniques were as described previously.^{2,3}

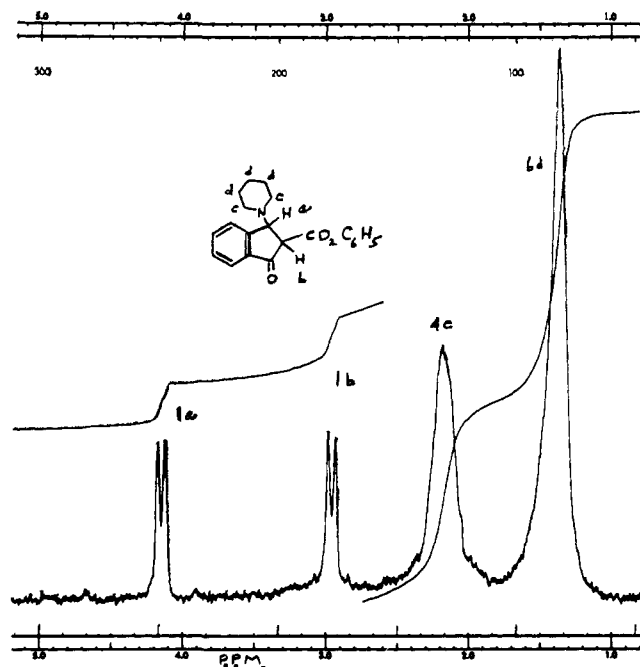


Fig. 1.—The proton magnetic resonance spectrum of 3-piperidino-2-(α,α -dideuteriobenzyl)-1-indanone.

Three illustrative runs are given in Table VI. The integrated second-order rate coefficients, k₂ (l. mole⁻¹ sec.⁻¹), are calculated with respect to the 2-bromoketone and to the additive.

Product Studies.¹⁶ Elimination from 2-Bromo-2-benzyl-1-indanone (IV). (a) **With Tetraethylammonium Bromide in Acetonitrile.**—A 60-ml. portion of a solution 0.0500 M in IV and 0.0764 M in tetraethylammonium bromide was maintained at

(16) Melting points were read with a calibrated thermometer. 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. The ultraviolet spectra were determined with a Cary Model 11-MS recording spectrophotometer using reagent grade methanol solutions. The proton magnetic resonance spectra were obtained with a Varian A-60 instrument using deuteriochloroform solutions containing a trace of tetramethylsilane (τ 10.00) as internal reference.

90.6° for 40 hr. A 5-ml. portion was removed and titration of acid development showed that 24.6 ml. of 0.0090 M sodium methoxide was required for neutralization. This corresponds to 90% of stoichiometrically possible acid formation.

The remaining 55-ml. portion was evaporated to dryness under reduced pressure and the residue washed with distilled water, filtered, and dried. Obtained was 0.556 g. (93% yield) of crude 2-benzal-1-indanone (V), m.p. 104–107°, $\gamma_{C=O}$ (7.1 mg./ml.) 1760/93. Recrystallization from methanol–water raised the m.p. to 109–110.5°.¹³

An attempt to prepare 2-(α -bromobenzyl)-1-indanone by addition of HBr to V in ether by the method found successful for addition to 4-biphenyl-1-cyclohexenyl ketone⁷ failed. Almost quantitative recovery was observed.

(b) **With Piperidine in Acetonitrile.**—A 0.470-g. sample of IV was heated at 61.5° with 0.650 g. of piperidine in 40 ml. of acetonitrile for 24 hr. The solvent was removed by evaporation under reduced pressure and the product washed with distilled water, filtered, and dried. Recrystallization from ethanol–water gave 0.285 g. (81% yield) of 2-benzal-1-indanone (V), m.p. 108–109°.

A solution of 0.30 g. of IV and 1.00 g. of piperidine in 25 ml. of acetonitrile was maintained at 90° for 2 hr. The solvent was removed by evaporation under reduced pressure and the product washed well with water. The proton magnetic resonance spectrum indicated the product to contain about 79% 2-benzal-1-indanone (V) and about 10% of 3-piperidino-2-benzyl-1-indanone (VI).

Elimination from 2-Bromo-2-(α,α -dideuteriobenzyl)-1-indanone (IVa). (a) **With Tetraethylammonium Bromide in Acetonitrile.**

—A solution of 0.50 g. of IVa and 1.00 g. of tetraethylammonium bromide in 30 ml. of acetonitrile was maintained at 90° for 64 hr. The solution was evaporated to dryness and the solid residue extracted with benzene. Evaporation of the benzene gave 0.37 g. of a product whose proton magnetic resonance spectrum was identical with that of 2-(α -deuteriobenzyl)-1-indanone¹⁷ (100% yield). The aromatic proton β to the carbonyl group is at 2.08 τ ($J = 7$ c.p.s.), eight aromatic protons occur in the range 2.2–2.8 τ , and the two methylene protons appear as a sharp singlet at 5.97 τ .

(b) **With Piperidine in Acetonitrile.**—A solution in acetonitrile of 0.30 g. of IVa and 0.40 g. of piperidine was heated at 90° for 5 hr. Evaporation to dryness and extraction with benzene left 0.16 g. of piperidine hydrobromide (100% yield). The benzene solution was evaporated to dryness to give an oil which was dried under vacuum. The proton magnetic resonance spectrum indicated a mixture of 47% of 2-(α -deuteriobenzyl)-1-indanone (Va) and 40% of 3-piperidino-2-(α,α -dideuteriobenzyl)-1-indanone (VIa).

The reaction was repeated maintaining 2.0 g. of IVa and 4.0 g. of piperidine in 40 ml. of acetonitrile at 90° for 4 hr. Evaporation to dryness, extraction with ether, water washing, and drying over anhydrous sodium sulfate was followed by the passing of dry hydrogen chloride into the solution. The precipitate was

(17) D. N. Kevill, G. A. Coppens, M. Coppens, and N. H. Cromwell; *J. Org. Chem.*, **29**, 382 (1964).

washed twice with ether and recrystallized from acetone to give colorless crystals of 3-piperidino-2-(α,α -dideuteriobenzyl)-1-indanone hydrochloride (VIIa), m.p. 210° dec.

Anal. Calcd. for $C_{21}H_{22}D_2NOCl$: C, 73.34; H, 7.10; N, 4.07; Cl, 10.31. Found: C, 73.30; H, 6.96; N, 4.07; Cl, 10.46.

The hydrogen analysis accounts for 6.45% hydrogen and 1.17% deuterium such that the calculated percentage of hydrogen as obtained by a routine analysis is 7.10%.

The proton magnetic resonance spectrum of 3-piperidino-2-(α,α -dideuteriobenzyl)-1-indanone (VIa), as derived from the above hydrochloride, shows nine aromatic protons in the range 2.0–3.0 τ and two protons splitting each other with a $J_{ax} = 3$ c.p.s. at 5.86 τ for the proton on the same carbon as the piperidino group and at 7.04 τ for the proton on the same carbon as the α,α -dideuteriobenzyl group. The signals from the protons of the

piperidino group occur as two broad peaks, one corresponding to four protons at 7.82 τ and one corresponding to six protons at 8.63 τ (Fig. 1).

(c) **With Piperidine in Benzene.**—A solution of 0.30 g. of IVa and 1.00 g. of piperidine in 40 ml. of benzene was maintained at 90° for 60 hr. A precipitate of 0.13 g. of piperidine hydrobromide (80% yield) was filtered off. The solution was evaporated under reduced pressure to give an oil. The proton magnetic resonance spectrum indicated that the oil contained 46% of 2-(α,α -dideuteriobenzyl)-1-indanone (Va) and 43% of 3-piperidino-2-(α,α -dideuteriobenzyl)-1-indanone (VIa).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE PENNSYLVANIA STATE UNIVERSITY, UNIVERSITY PARK, PENNSYLVANIA]

Pyrolysis of *sec*-Butyl Acetate. Stereospecific *cis* Elimination¹

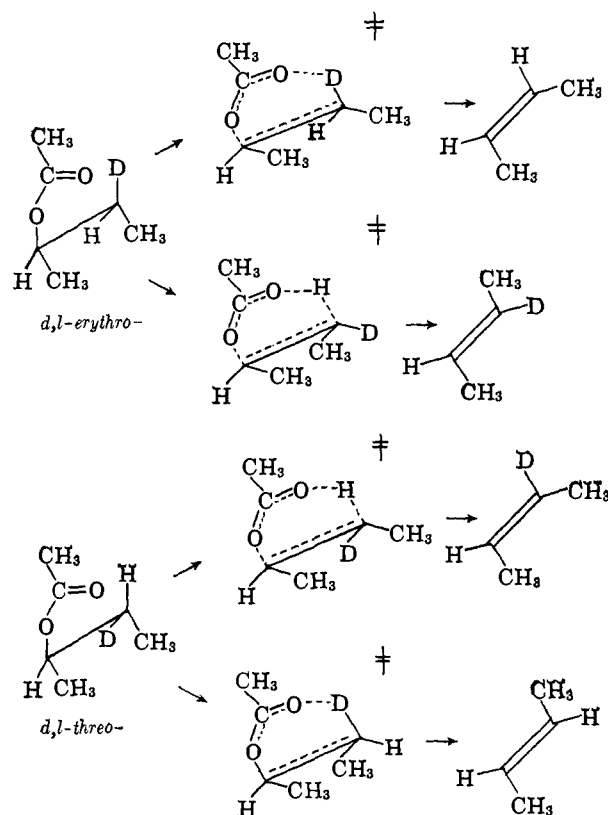
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The acetates of *d,l*-threo- and *d,l*-erythro-3-deuterio-2-butanol were pyrolyzed at 400°. Both *cis*- and *trans*-2-butenes were formed in stereospecific *cis* eliminations.

The cyclic intramolecular mechanism for the pyrolyses of esters having β -H, as first proposed by Hurd and Blunck,² has been generally accepted. The strongest evidence in support of the mechanism for this vapor phase decomposition as well as those of amine oxides,^{3a} xanthates,^{3b} and chloroformates⁴ has resulted from stereochemical studies.⁵ In all cases the predominant olefinic products are the result of the expected *cis* eliminations. However, there are produced during the acetate pyrolyses differing amounts of olefins which are not the result of *cis* eliminations. When *cis*-2-methylcyclohexyl acetate was decomposed in the vapor phase at 500°, Arnold, Smith, and Dodson⁶ found 1-methylcyclohexene as 25% of the olefinic products. Alexander and Mudrak⁷ found 7.2% 1-phenylcyclohexene in the olefins produced when *cis*-2-phenylcyclohexyl acetate was pyrolyzed at 600°. Similar results were obtained when Curtin and Kellom⁸ studied the stereochemistry of pyrolytic elimination in an acyclic system. The acetate of *d,l*-threo-2-deuterio-1,2-diphenylethanol was pyrolyzed at 400° and the resulting *trans*-stilbene was 26% monodeuterated. In all these studies significant amounts of olefins were produced which did not result from a *cis* elimination. The cyclic intramolecular mechanism is not compatible with these products and a second reaction path must be operating if these are the primary products. Since it is not clear that the earlier studies excluded the possibility that the primary products were not stable under the reaction conditions, the *sec*-butyl system was investigated with the expectation of avoiding this difficulty.

The acetates of *d,l*-erythro- and *d,l*-threo-3-deuterio-2-butanol were pyrolyzed at 400° to investigate the stereochemistry of elimination in the *sec*-butyl system. The products expected *via* a cyclic transition state are shown in the reaction schemes.



The butenes produced were analyzed, separated, and purified by vapor phase chromatography. The individual fractions were then analyzed by mass spectrometry at low voltages. The heights of the parent peaks for masses 56 and 57 were taken as a measure of the relative amounts of undeuterated and

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