# Elimination Reactions of α-Halogenated Ketones. XIII.[1] Substituent Effects upon the Kinetics and Mechanism of Halide Ion Promoted Dehydrobromination of Derivatives of 2-Benzyl-2-bromo-1-indanone in Acetonitrile[2]

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**Abstract:** The effect of *para* substituents within the aromatic ring of the benzyl group upon the kinetics of the bimolecular halide ion promoted dehydrobromination of 2-benzyl-2-bromo-1-indanone is quite mild; the "averaged" Hammett ρ is positive but of much lower value than that previously found for alkoxide-promoted eliminations of various β-phenylethyl compounds in alcohols. Although our Hammett plots differ in character from those obtained in previous elimination studies, there are remarkably good correlations with Hammett plots based upon previous studies, in acetone, of iodide substitutions within various *para*-substituted β-phenylethyl chlorides and phenyl chloromethyl ketones. The low ρ values, coupled with low deuterium isotope effects and extreme sensitivity to the nature of the leaving group, give further support to the generally accepted view that in the transition states for suitable bimolecular eliminations carbon–halogen bond breaking is running considerably ahead of carbon–hydrogen bond breaking. As the Hammett σ value for the *para* substituent increases, so also does the rate of attack by chloride ion relative to that by bromide ion; at 60°, the ratio rises from 16 for *p*-methoxy to 53 for *p*-nitro. Deuterium isotope effects previously reported for 2-benzyl-2-bromo-1-indanone have been extended to the 3,3-dimethyl derivative. Seventeen new indanone derivatives have been prepared and characterized.

In this series of papers it has been shown that bimolecular dehydrohalogenations of several tertiary α-halogenated ketones proceed through a transition state in which carbon–halogen bond breaking is running ahead of carbon–hydrogen bond breaking. The evidence presented has included demonstration of low deuterium isotope effects, coupled with high sensitivity to the identity of the leaving halogen.[1] Since little is known concerning the precise topology, charge distribution, and bonding within transition states for bimolecular eliminations, a more detailed description is necessarily somewhat speculative.

We have favored a mechanism in which approach of the nucleophilic reagent can assist in the elongation of the carbon to halogen bond by direct interaction, in addition to any effect transmitted *via* the β-hydrogen, with the possibility in suitable cases of elongation of the carbon to halogen bond prior to nucleophilic attack.[4] At some stage in the mechanism interaction between the nucleophile and a β-hydrogen becomes dominant and the reaction leads to an elimination product; in other cases, extensive interaction with a β-hydrogen never develops and these reactions lead to substitution.

The mechanism for bimolecular elimination from α,α-dimethylphenylethyl chloride, where there is also strong evidence that carbon–halogen bond breaking is running ahead of carbon–hydrogen bond breaking, has been described as resembling a classical E2 mechanism with superimposed E1 character.[5] For this type of mechanism, interactions involving the attacking reagent are felt only *via* the β-hydrogen.
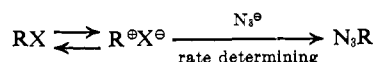
Subsequent to our immediately preceding publication,[1] two contributions have emerged from other laboratories which support certain essential features of our mechanism. The most striking, as regards our mechanism, is a study by Lemieux and Lineback[6] of the dehydrobromination of tetra-*O*-acetyl-α-D-glucopyranosyl bromide in acetonitrile as promoted by amines and tetraalkylammonium salts, reaction conditions being essentially identical with those of our studies. Kinetic and product studies were very well rationalized in terms of a merged bimolecular substitution and elimination mechanism in which considerable ionic character, resulting from dipolar development within the carbon–bromine bond, was incorporated. Their scheme is extremely similar, and, in most essentials, identical with our earlier proposal.[4]

Also, Weiner and Sneen[7] have proposed that certain reactions, formally represented as SN2, are not synchronous displacements but involve rate-determining nucleophilic attack upon an activated intermediate. This is in accord with the formulation,[4] for suitable structures, of considerable dipolar development prior to attack by the nucleophile. Indeed, Weiner and Sneen postulate that their reactions are SN2C+ in character, attack being upon an equilibrium concentration of a preformed ion-pair intermediate.[8]

(1) For paper XII in this series, see D. N. Kevill, G. A. Coppens, and N. H. Cromwell, *J. Am. Chem. Soc.*, **86**, 1553 (1964).

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(3) (a) Abstracted in part from the Ph.D. dissertation of E. D. W., submitted in Jan 1966; (b) author to whom communications should be addressed.

(4) (a) D. N. Kevill and N. H. Cromwell, *Proc. Chem. Soc.*, 252 (1961); (b) *J. Am. Chem. Soc.*, **83**, 3815 (1961).

(5) J. F. Bunnett, G. T. Davis, and H. Tanida, *ibid.*, **84**, 1606 (1962).

(6) R. U. Lemieux and D. R. Lineback, *Can. J. Chem.*, **43**, 94 (1965).

(7) (a) H. Weiner and R. A. Sneen, *J. Am. Chem. Soc.*, **87**, 287 (1965); (b) *ibid.*, **87**, 292 (1965). See also R. A. Sneen and J. W. Larsen, Abstracts of Papers, 150th National Meeting of American Chemical Society, Atlantic City, N. J., Sept 1965, p 41S.

(8) Applying the principle of microscopic reversibility to the scheme proposed by Weiner and Sneen[7a]

$$RX \rightleftarrows R^{\oplus}X^{\ominus} \xrightarrow[\text{rate determining}]{N_3^{\ominus}} N_3R$$

it would seem that the formulation must be extended at least as far as to

This communication reports upon various substituent effects in the dehydrobromination reactions of derivatives of 2-benzyl-2-bromo-1-indanone (I). The effect of substitution of two methyl groups in the 3 position upon the rate of elimination as promoted by piperidine, bromide, and chloride has been investigated both for I and for its *p*-chloro derivative. Previous deuterium isotope effects upon bromide ion promoted dehydrobromination of I have been supplemented by parallel measurements for 2-benzyl-2-bromo-3,3-dimethyl-1-indanone (II). The major contribution is, however, a study of the effect of *para* substituents within I upon the rates of dehydrobromination as promoted by chloride and by bromide. Hammett σ–ρ correlations are, for elimination reactions, extremely sparse and appear to have been available previously only for eliminations from β-phenylethyl compounds as promoted by alkoxide in alcoholic media,[9,10] eliminations which are generally accepted to be on the carbanion side of a synchronous E2 elimination.[11] Our study appears to be the first in which Hammett σ–ρ correlations have been obtained for an elimination reaction in which carbon–hydrogen bond breaking is thought to be little developed in the transition state and, also, the first for elimination reactions carried out in an aprotic solvent.
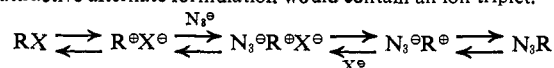
### Kinetic Results[12]

It was found that, under the appropriate reaction conditions, acetonitrile solutions of the α-bromoindanones used in this investigation developed no more than marginal acidity during the time periods over which the dehydrobrominations were studied.[1]

**Halide Ion Promoted Dehydrobromination of *para*-Substituted 2-Benzyl-2-bromo-1-indanones and 2-Benzyl-2-bromo-3,3-dimethyl-1-indanones in Acetonitrile.** Halide ion was supplied as the appropriate tetraethylammonium salt. The extent of reaction was followed by titration of the acid developed. The first-order rate coefficients with respect to the α-bromoindanone fell as the reaction proceeded owing to complexing of halide ion by developing hydrogen halide, with formation of triple ions. Initial values were obtained by extrapolation to zero extent of reaction; from these the initial second-order rate coefficients with respect to bromoindanone and tetraethylammonium salt were calculated.

accommodate an ion pair as the immediate product resulting from azide attack.

$$RX \rightleftharpoons R^{\oplus}X^{\ominus} \underset{X^{\ominus}}{\overset{N_3^{\ominus}}{\rightleftharpoons}} N_3^{\ominus}R^{\oplus} \rightleftharpoons N_3R$$
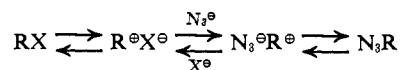
An attractive alternate formulation would contain an ion triplet.

$$RX \rightleftharpoons R^{\oplus}X^{\ominus} \overset{N_3^{\ominus}}{\rightleftharpoons} N_3^{\ominus}R^{\oplus}X^{\ominus} \underset{X^{\ominus}}{\rightleftharpoons} N_3^{\ominus}R^{\oplus} \rightleftharpoons N_3R$$

The latter scheme, leading to substitution, constitutes one extreme of our spectrum of merged substitution and elimination mechanisms,[4] an extreme in which bond breaking is completed prior to approach of the nucleophile.

(9) (a) C. H. Depuy and D. H. Froemsdorf, *J. Am. Chem. Soc.*, **79**, 3710 (1957); (b) W. H. Saunders, Jr., and R. A. Williams, *ibid.*, **79**, 3712 (1957).

(10) (a) C. H. DePuy and C. A. Bishop, *ibid.*, **82**, 2532 (1960); (b) *ibid.*, **82**, 2535 (1960).

(11) For two recent reviews bringing together the evidence for this belief, see (a) C. K. Ingold, *Proc. Chem. Soc.*, 265 (1962); (b) J. F. Bunnett, *Angew. Chem. Intern. Ed. Engl.*, **1**, 225 (1962).

(12) The rate coefficients reported within this paper are not corrected for expansion of the solvent from room temperature to reaction temperature.

**Scheme I**



G = H or CH₃
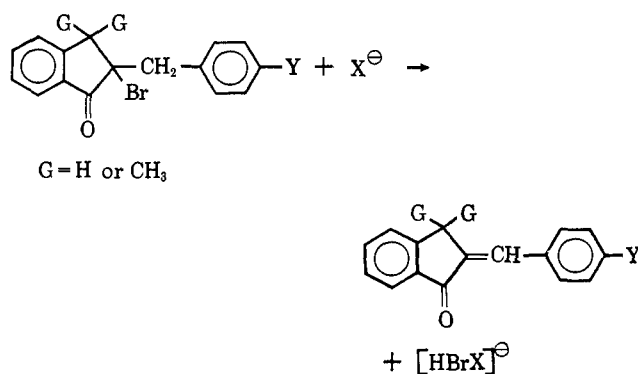
The kinetic data, as reported in Tables I and II, give mean values for the initial second-order rate coefficients for each system at each temperature. The values quoted are the mean of from two to four determinations at varying reactant concentrations (within the range 0.004 to 0.05 *M*). Almost without exception, all the initial second-order rate coefficients for a given system at a given temperature were within 5% of each other; in most cases the agreement was somewhat better.

**Table I.** Mean Values for Initial Second-Order Rate Coefficients, $k_2$ (l. mole$^{-1}$ sec$^{-1}$), for Halide Ion Promoted Dehydrobromination of *para*-Substituted 2-Benzyl-2-bromo-1-indanones

| Temp, °C | X[a] | Y[a] | $10^4 k_2$ | Temp, °C | X[a] | Y[a] | $10^4 k_2$ |
|---|---|---|---|---|---|---|---|
| 45.1 | Cl | OCH₃ | 9.1 | 47.3 | Cl | Cl | 17.2 |
| 55.9 | Cl | OCH₃ | 27.1 | 50.2 | Cl | Cl | 23.1 |
| 65.6 | Cl | OCH₃ | 66 | 60.8 | Cl | Cl | 61 |
| 75.6 | Cl | OCH₃ | 156 | 67.0 | Cl | Cl | 112 |
| 65.9 | Br | OCH₃ | 3.9 | 74.9 | Cl | Cl | 229 |
| 79.9 | Br | OCH₃ | 14.5 | 59.7 | Br | Cl | 2.00 |
| 89.9 | Br | OCH₃ | 34.4 | 70.6 | Br | Cl | 6.2 |
| 98.9 | Br | OCH₃ | 71 | 80.5 | Br | Cl | 15.8 |
| 41.2 | Cl | CH₃ | 5.9 | 90.0 | Br | Cl | 35.2 |
| 49.6 | Cl | CH₃ | 14.8 | 95.9 | Br | Cl | 58 |
| 59.6 | Cl | CH₃ | 41 | 28.2 | Cl | NO₂ | 6.0 |
| 68.1 | Cl | CH₃ | 83 | 44.7 | Cl | NO₂ | 37.6 |
| 71.6 | Br | CH₃ | 7.4 | 52.4 | Cl | NO₂ | 83 |
| 80.0 | Br | CH₃ | 14.9 | 61.8 | Cl | NO₂ | 201 |
| 89.2 | Br | CH₃ | 36.1 | 70.9 | Br | NO₂ | 10.0 |
| 99.7 | Br | CH₃ | 83 | 80.7 | Br | NO₂ | 25.5 |
| 39.9 | Cl | H | 4.8 | 91.4 | Br | NO₂ | 66 |
| 49.2 | Cl | H | 13.8 | 98.9 | Br | NO₂ | 136 |
| 59.7 | Cl | H | 37.4 | | | | |
| 64.3 | Cl | H | 86 | | | | |
| 75.6 | Cl | H | 171 | | | | |
| 60.0 | Br | H | 1.47[b] | | | | |

[a] See Scheme I (G = H). [b] See ref 1 for additional data on this system.

**Piperidine-Promoted Dehydrobromination of 2-Benzyl-2-bromo-3,3-dimethyl-1-indanone in Acetonitrile.** The reaction was followed in terms of the rate of appearance of bromide ion, with initial reactant concentrations in the range 0.01 to 0.2 *M*. The integrated second-order rate coefficients, first order in each reactant, were constant over at least 80% stoichiometrically possible reaction. The data are summarized in Table III.

### Analysis of Results

**Effect on Reaction Rate of Introducing Two 3,3-Dimethyl Groups.** A graphical comparison of the

**Table II.** Mean Values for Initial Second-Order Rate Coefficients, $k_2$ (l. mole$^{-1}$ sec$^{-1}$), for Halide Ion Promoted Dehydrobromination of *para*-Substituted 2-Benzyl-2-bromo-3,3-dimethyl-1-indanones

| Temp, °C | X[a] | Y[a] | $10^4 k_2$ | Temp, °C | X[a] | Y[a] | $10^4 k_2$ |
|---|---|---|---|---|---|---|---|
| 62.0 | Cl | H | 7.6 | 89.9 | Br | H | 2.25[c] |
| 62.5 | Cl | H | 8.8 | 98.3 | Br | H | 6.5[c] |
| 74.1 | Cl | H | 24.4 | 50.2 | Cl | Cl | 3.9 |
| 91.9 | Cl | H | 103 | 60.3 | Cl | Cl | 10.6 |
| 61.5 | Br | H | 0.33 | 71.6 | Cl | Cl | 34.2 |
| 74.1 | Br | H | 1.04 | 81.4 | Cl | Cl | 90 |
| 90.6 | Br | H | 5.5 | 81.4 | Br | Cl | 3.8 |
| 99.6 | Br | H | 15.3 | 91.3 | Br | Cl | 9.7 |
| 106.5 | Br | H | 24.5[b] | 100.4 | Br | Cl | 22.3 |
| 74.0 | Br | H | 0.42[c] | 108.1 | Br | Cl | 46 |

[a] See Scheme I (G = CH₃). [b] Also followed in terms of increase in bromide ion concentration, $k_2 = 24.8 \times 10^{-4}$ l. mole$^{-1}$ sec$^{-1}$. [c] These runs carried out using 2-($\alpha,\alpha$-dideuteriobenzyl)-2-bromo-3,3-dimethyl-1-indanone.

**Table III.** Mean Second-Order Rate Coefficients, $k_2$ (l. mole$^{-1}$ sec$^{-1}$), for Piperidine-Promoted Dehydrobromination of 2-Benzyl-2-bromo-3,3-dimethyl-1-indanone

| Temp, °C | 43.8 | 60.0 | 74.1 |
|---|---|---|---|
| $10^4 k_2$ | 3.8[a] | 10.7[a] | 24.3[b] |

[a] Mean of two runs. [b] Mean of three runs; also followed by measurement of piperidine neutralization, $k_2 = 21.3 \times 10^{-4}$ l. mole$^{-1}$ sec$^{-1}$.

rates of reaction of 2-benzyl-2-bromo-1-indanone, 2-(*p*-chlorobenzyl)-2-bromo-1-indanone, and the corresponding 3,3-dimethyl compounds with piperidine, bromide, or chloride allows deduction of the effect of the two 3-position methyl groups upon the rates of attack by each reagent at any temperature within the range studied. Details of an analysis of this type are given in Table IV.

**Table IV.** Rate of Reaction of 2-Benzyl-2-bromo-1-indanones (A) Relative to the Rate for the Corresponding 2-Benzyl-2-bromo-3,3-dimethyl-1-indanone (B)

| Temp, °C | *para* Substituent | Reagent | A/B |
|---|---|---|---|
| 40 | H | C₅H₁₁N | 11[a] |
| 60 | H | C₅H₁₁N | 9.0[a] |
| 80 | H | Br⁻ | 6.1[a] |
| 90 | H | Br⁻ | 5.4[a] |
| 60 | H | Cl⁻ | 6.5 |
| 70 | H | Cl⁻ | 5.6 |
| 80 | Cl | Br⁻ | 4.8 |
| 90 | Cl | Br⁻ | 4.0 |
| 60 | Cl | Cl⁻ | 5.6 |
| 70 | Cl | Cl⁻ | 4.8 |

[a] Data for 2-benzyl-2-bromo-1-indanone from ref 1.

For all the systems studied introduction of the two methyl groups leads to a reduced elimination rate. An additional primary steric hindrance to reagent participation is suggested by the retardation being felt: C₅H₁₁N > Br⁻ > Cl⁻. However, the effect is less in the presence of a *p*-chloro substituent, indicating a more complex over-all situation. If, as shall be developed later, the detailed topology of the transition state is dependent upon the identity of the *para* substituent, then observation of a *para* substituent effect indicates that steric effects dependent upon the detailed topology

of bimolecular dehydrobromination transition states are accompanying the introduction of the 3,3-dimethyl groups. That specific interactions are plausible, indeed probable, is indicated by previous ultraviolet[13] and equilibration[14] studies on *cis*- and *trans*-2-benzyl-3,3-dimethyl-1-indanone; a molecular model suggests an interaction in the *trans* isomer between one of the methyl groups and a hydrogen of the benzylic aromatic ring.[13] Presumably these steric effects will be felt to some extent within the transition states of reactions leading to formation of the $\alpha,\beta$-unsaturated ketone.

**Deuterium Isotope Effects in Bromide Ion Promoted Dehydrobromation of 2-Benzyl-2-bromo-3,3-dimethyl-1-indanone.** The rate of elimination from 2-($\alpha,\alpha$-dideuteriobenzyl)-2-bromo-3,3-dimethyl-1-indanone has been compared to that for the nondeuterated compound. Reaction was promoted by bromide ion, and the study is strictly parallel to the one previously reported for 2-($\alpha,\alpha$-dideuteriobenzyl)-2-bromo-1-indanone.[1] An analysis is given in Table V.

**Table V.** Deuterium Isotope Effects upon the Initial Second-Order Rate Coefficients, $k_2$ (l. mole$^{-1}$ sec$^{-1}$), for Bromide Ion Promoted Dehydrobromination of 2-Benzyl-2-bromo-3,3-dimethyl-1-indanone

| Temp, °C | $10^4 k_2^{H}$ [a] | $10^4 k_2^{D}$ [b] | $k_2^{H}/k_2^{D}$ |
|---|---|---|---|
| 74.0 | 1.03 ± 0.06[c] | 0.42 ± 0.02 | 2.5 ± 0.3 |
| 89.9 | 5.2 ± 0.2[c] | 2.25 ± 0.10 | 2.3 ± 0.2 |
| 98.3 | 13.2 ± 0.5[c] | 6.5 ± 0.2 | 2.0 ± 0.2 |

[a] For 2-benzyl-2-bromo-3,3-dimethyl-1-indanone. [b] For 2-($\alpha,\alpha$-dideuteriobenzyl)-2-bromo-3,3-dimethyl-1-indanone. [c] By interpolation within the data of Table II.

The ratios are low, consistent with the results for 2-benzyl-2-bromo-1-indanone.[1] We interpret these low ratios as previously; *i.e.*, we believe that they indicate less carbon–hydrogen bond breaking than in the transition state for a fully synchronous E2 elimination. Introduction of the two methyl substituents further reduces the already low isotope effect; *e.g.*, the value of 2.3 at 89.9° can be compared to 2.8 at 89.8° for the nonmethylated compound.[1] Presumably, the extent of carbon–hydrogen bond breaking in the transition state is also further reduced.

**Effect of *para* Substituents on the Rates of Halide Ion Promoted Dehydrobrominations of 2-Benzyl-2-bromo-1-indanone.** The rates for 60 and 80°, presented in Table VI, were obtained graphically using the data of Table I.

Hammett plots based upon the data of Table VI are shown in Figure 1. Both of the plots based on $\sigma$ values are curved concave upwards and although the approximation to linearity is better when the $\sigma^*$ value is used for *p*-nitro, as suggested by Saunders and Williams,[9b] the correlation is still poor. These curved plots are further examples of a type of plot which is already widely recognized,[15] and the curvature is usually considered to arise from varying transition state structure; these variations cause $\rho$ to vary with the $\sigma$ value for the substituent.

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

(14) D. N. Kevill, E. D. Weiler, and N. H. Cromwell, *ibid.*, **29**, 1276 (1964).

(15) See, for example, J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, p 187.
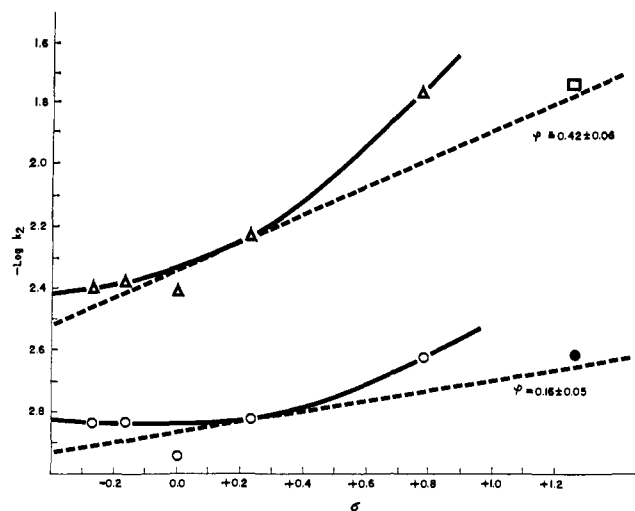
Figure 1. Hammett $\sigma$–$\rho$ plots of initial second-order rate coefficients, $k_2$ (1. mole$^{-1}$ sec$^{-1}$), for halide ion promoted dehydrobromination of *para*-substituted 2-benzyl-2-bromo-1-indanones in acetonitrile; O, Br$^-$ at 80°; △, Cl$^-$ at 60°. From left to right, the *para* substituents are $OCH_3$, $CH_3$, H, Cl, $NO_2$. The points at the extreme right (● and □) are based upon the $\sigma^*$ value for *p*-$NO_2$. The slopes and standard deviations, $\rho \pm S_\rho$, are calculated using the $\sigma^*$ value (and not the $\sigma$ value) for *p*-$NO_2$.

The "averaged" $\rho$ values obtained by a least-squares fit are, for chloride ion promoted elimination, $+0.42 \pm 0.06$, and, for bromide ion promoted elimination, $+0.16 \pm 0.05$. These values, although not very meaningful in a quantitative sense, are considerably less than
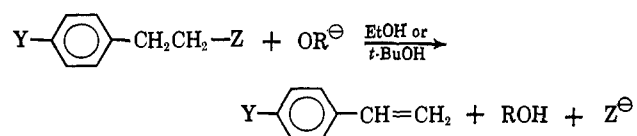
Table VI. Effect of *para* Substituents on the Initial Second-Order Rate Coefficients, $k_2$ (1. mole$^{-1}$ sec$^{-1}$), for Halide Ion Promoted Dehydrobromination of 2-Benzyl-2-bromo-1-indanone

| $Y^a$ | $\sigma^b$ | $10^4 k_2^{Br^-}$ (60°)$^c$ | $10^4 k_2^{Br^-}$ (80°)$^d$ | $10^4 k_2^{Cl^-}$ (60°)$^e$ | $k_2^{Cl^-}$ (60°)/ $k_2^{Br^-}$ (60°) |
|---|---|---|---|---|---|
| $OCH_3$ | $-0.268$ | 2.4 | 14.7 | 39 | 16 |
| $CH_3$ | $-0.170$ | 2.4 | 14.9 | 42 | 18 |
| H | 0.0000 | 1.5 | 11.5$^f$ | 39$^g$ | 26 |
| Cl | $+0.227$ | 2.0 | 15.2$^h$ | 58$^i$ | 29 |
| $NO_2$ | $+0.778$ | 3.2 | 23.7 | 170 | 53 |

$^a$ See Scheme I (G = H). $^b$ Hammett $\sigma$ values from compilation by H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953); $\sigma^*$ value for *p*-$NO_2$ from same source is 1.270. $^c$ By extrapolation, reagent is bromide ion at 60°. $^d$ By interpolation, reagent is bromide ion at 80°. $^e$ By interpolation, reagent is chloride ion at 60°. $^{f-i}$ Values for the corresponding 3,3-dimethyl derivative (Scheme I, G = $CH_3$) are as follows: $^f$ 1.9, $^g$ 6.0, $^h$ 3.2, $^i$ 10.3.

the "averaged" $\rho$ values for ethoxide or *t*-butoxide promoted eliminations from various *para*-substituted $\beta$-phenylethyl compounds (Scheme II).

Scheme II

$$Y-\langle\bigcirc\rangle-CH_2CH_2-Z + OR^\ominus \xrightarrow[\text{t-BuOH}]{\text{EtOH or}}$$

$$Y-\langle\bigcirc\rangle-CH=CH_2 + ROH + Z^\ominus$$

In these reactions the $\rho$ values were found to be positive and within, or occasionally just outside, the range of 2–3.[8–10] The bromide (Scheme II, Z = Br) reacted

with ethoxide in ethanol with a $\rho$ of $+2.14$, and the deuterium isotope effect for this system, 7.1,[16] suggests about one-half transfer of the hydrogen (deuterium) in the transition state. As Z is varied to more electronegative groups the isotope effect falls and the $\rho$ value rises, consistent with increased carbanion character in these reactions.[11] The low deuterium isotope effects for halide ion promoted dehydrobromination of tertiary $\alpha$-bromoindanones in acetonitrile are accompanied by *the $\rho$ values being considerably reduced below those for reactions having about half-transfer of hydrogen in the transtion state* (as indicated by deuterium isotope effects and $\rho$ values for $\beta$-phenylethyl compounds). This is consistent with the view, already advanced on other grounds,[1] that the transition states involve carbon–bromine bond breaking running ahead of carbon–hydrogen bond breaking rather than a trend toward development of carbanion character.

The curvature of the Hammett plots is reminiscent of a similar curvature for the plot representing ethoxide ion promoted elimination from *para*-substituted $\beta$-phenylethyl bromides in ethanol[9b] (when based on $\sigma$ rather than $\sigma^*$ values). However, while all the derivatives in the previous study[9b] lay nicely on a smooth curve, we obtain smooth curves only by ignoring the points for the unsubstituted compound. There is considerable precedent for constructing the curves in this way and Swain and Langsdorf[17] have discussed several examples of reactions for which two curves are required: one for when *para* substituents are present and one, with lower rates, for *meta* substituents or no substituents (as in the present case).[18]

Considering our curved $\sigma$–$\rho$ plots in conjuction with those of Saunders and Williams,[9b] it appears that not only do gross transition-state structures for bimolecular eliminations vary greatly but the detailed topology, charge distribution, and bonding within the transition state is, for a given reaction type, very dependent upon the exact nature of the reactants. The differing "averaged" $\rho$ values for chloride and bromide ion attack show that this argument applies equally to both substrate and reagent.

A direct comparison of the rates of attack by chloride relative to bromide upon a given substrate (column 6 of Table VI) shows that the ratio rises steadily in moving from strongly electron-supplying to strongly electron-withdrawing *para* substituents (Y in Scheme I); for example, at 60° it rises from 16 for *p*-methoxy to 53 for *p*-nitro.

Evidence for systematic variation in transition-state structure dependent upon the electronegativity of the leaving group has recently been reviewed[11] and, more recently, the effect of leaving group electronegativity in $\alpha,\alpha$-dimethylphenylethyl compounds, upon the relative rates of elimination as promoted by thioethoxide and methoxide, has been shown to be such that the poorer the leaving group the more attack by methoxide was favored relative to attack by thioethoxide.[19] These variations in the relative effectiveness of two nucleophiles (bases), with the nature of the leaving group and with the nature of substituents within a $\beta$-aromatic ring,

(16) W. H. Saunders, Jr., and D. H. Edison, *J. Am. Chem. Soc.*, **82**, 138 (1960).
(17) C. G. Swain and W. P. Langsdorf, Jr., *ibid.*, **73**, 2813 (1951).
(18) For more recent examples and discussion, see ref 15, p 190.
(19) J. F. Bunnett and E. Baciocchi, *Proc. Chem. Soc.*, 238 (1963).

are consistent with a merged mechanism in which nucleophilicities toward both carbon and hydrogen have to be considered and with the dependence upon each of the two nucleophilicities correlating with detailed transition-state structure. A poor leaving group or an electron-withdrawing substituent in a $\beta$-aromatic ring would be expected to favor increased bonding to $\beta$-hydrogen within the transition state.

One system cited by Swain and Langsdorf,[17] in their discussion of the type of Hammett $\sigma$-$\rho$ plot which is both curved and accompanied by increased transition-state stability when *para* substituted, was the bimolecular *substitution* reaction of $\beta$-phenylethyl chloride with iodide ion in acetone at 75°;[20] the data also have been presented as a Hammett $\sigma$-$\rho$ plot by DePuy and Bishop.[10a] Although, because of curvature, the cor-

$$Y-\langle\bigcirc\rangle-CH_2CH_2Cl + I^\ominus \xrightarrow[75°]{acetone}$$

$$Y-\langle\bigcirc\rangle-CH_2CH_2I + Cl^\ominus$$
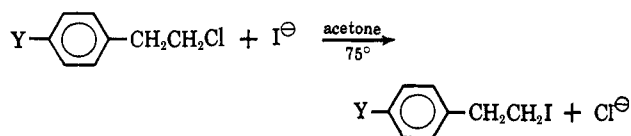
relation is poor, a $\rho$ value of +0.59 has been calculated.[21a] If (so as to make comparison) the $\sigma^*$ value is used for *p*-nitro, the $\rho$ value becomes approximately +0.4 (of the same order of magnitude as the values obtained in our elimination reactions). Also, the curvatures are very similar and in both studies the rate for the unsubstituted compound causes it to lie below the plot based on the rates for *para*-substituted compounds. It can be shown from a recent study[21b] that the iodide substitution reactions of *para*-substituted phenyl chloromethyl ketones, in acetone at 0°, have similar characteristics. A Hammett plot of the relative rates (based on the $\sigma^*$ value for *p*-nitro and neglecting the point for the unsubstituted compound) leads to a $\rho$ value of 0.61 ± 0.04.

While these similarities do not necessarily present evidence in favor of substitution character within our dehydrobrominations, there is certainly a parallel insofar as that each *para* substituent introduced into the $\beta$-phenyl group is, in the transition state, given a quantitative opportunity to interact with the rest of the system in a very similar manner for both the halide ion substitution reactions of $\beta$-phenylethyl chloride[20] and phenyl chloromethyl ketone[21b] in acetone and the halide ion promoted elimination reaction of 2-benzyl-2-bromo-1-indanone in acetonitrile.

## Experimental Section[22]

**Materials.** Piperidine,[4b] tetraethylammonium bromide,[23] and tetraethylammonium chloride[24] were purified as described previously. The acetonitrile was Eastman Kodak Co. Spectrograde.

(20) G. Baddeley and G. M. Bennett, *J. Chem. Soc.*, 1819 (1935).
(21) (a) H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953); (b) F. G. Bordwell and W. T. Brannen, Jr., *J. Am. Chem. Soc.*, **86**, 4645 (1964).
(22) Melting points were read with a calibrated thermometer. Ultraviolet spectra were determined with a Cary Model 11-MS recording spectrophotometer using reagent grade methanol solutions. Infrared spectra were determined with a Perkin-Elmer Model 21 double-beam recording instrument employing sodium chloride optics and matched sodium chloride cells with either carbon tetrachloride or chloroform solutions. Proton magnetic resonance spectra were also obtained and were in each case consistent with the proposed structure. These spectra showed interesting features which will be the subject of a future publication; details are also available in the Ph.D. thesis of E. D. W. The exocyclic $\alpha,\beta$-unsaturated ketones were assigned as *trans* or *cis* on the basis of their proton magnetic resonance spectra.[14] Analyses were by Microtech Analytical Laboratory, Skokie, Ill. Molecular weights were

**General Procedure for Preparation of the $\alpha$-Bromoindanones.** With the exception of 2-(*p*-nitrobenzyl)-2-bromo-1-indanone, the $\alpha$-bromoindanones were prepared *via* the corresponding $\alpha,\beta$-unsaturated ketones which were then hydrogenated and brominated. The sequential preparations of 2-benzyl-2-bromo-1-indanone (I)[25,26] and 2-benzyl-2-bromo-3,3-dimethyl-1-indanone (II)[13] have been described previously. Corresponding *para*-substituted derivatives were prepared by essentially identical techniques: 1-indanone or 3,3-dimethyl-1-indanone[13] was condensed with the appropriate *para*-substituted benzaldehyde, and the $\alpha,\beta$-unsaturated ketone formed was quantitatively hydrogenated across the olefinic bond, in dioxane or ethyl acetate, followed by bromination by the method of Leuchs.[27] Each step usually had a better than 80% yield. The characterization of new compounds involved in these sequential preparations is reported below.

*trans*-2-(*p*-Methoxybenzal)-1-indanone (III). Condensation of 1-indanone and *p*-methoxybenzaldehyde and recrystallization of the product from benzene gave colorless crystals: mp 138–139°; in $CHCl_3$, $\nu_{C=O}$ 1695 (s), $\nu_{C=C}$ 1633 (s), $\nu_{Ar}$ 1608 (s) cm$^{-1}$.
*Anal.* Calcd for $C_{17}H_{14}O_2$: C, 81.55; H, 5.64. Found: C, 81.62; H, 5.60.

2-(*p*-Methoxybenzyl)-1-indanone (IV). Hydrogenation of III in dioxane and recrystallization of the product from cyclohexane gave white crystals: mp 60–61°; in $CCl_4$, $\nu_{C=O}$ 1716 (s), $\nu_{Ar}$ 1615 (m) cm$^{-1}$; $\lambda_{max}$ 285 m$\mu$ ($\epsilon$ 4130), 245 (14,900), 225 (15,100).
*Anal.* Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 80.89; H, 6.47.

2-(*p*-Methoxybenzyl)-2-bromo-1-indanone (V). Bromination of IV and recrystallization of the product from aqueous ethanol gave white crystals: mp 77–78°; in $CCl_4$, $\nu_{C=O}$ 1728 (s), $\nu_{Ar}$ 1615 (s) cm$^{-1}$; $\lambda_{max}$ 300 m$\mu$ ($\epsilon$ 2610), 256 (12,200), 225 (16,700).
*Anal.* Calcd for $C_{17}H_{15}O_2Br$: C, 61.66; H, 4.54; Br, 24.13. Found: C, 61.55; H, 4.57; Br, 24.07.

*trans*-2-(*p*-Methylbenzal)-1-indanone (VI). Condensation of 1-indanone and *p*-methylbenzaldehyde and recrystallization of the product from aqueous methanol gave white crystals: mp 137–138°; in $CCl_4$, $\nu_{C=O}$ 1693 (s), $\nu_{C=C}$ 1629 (s), $\nu_{Ar}$ 1611 (s) cm$^{-1}$; $\lambda_{max}$ 331 m$\mu$ ($\epsilon$ 28,300), 278 (sh) (7720), 234 (9800).
*Anal.* Calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 87.19; H, 6.09.

2-(*p*-Methylbenzyl)-1-indanone (VII). Hydrogenation of VI in dioxane and recrystallization of the product from aqueous methanol gave white crystals: mp 50–51°; in $CCl_4$, $\nu_{C=O}$ 1715 (s), $\nu_{Ar}$ 1614 (m) cm$^{-1}$; $\lambda_{max}$ 291 m$\mu$ ($\epsilon$ 2950), 276 (sh) (2200), 246 (13,600).
*Anal.* Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.38; H, 6.92.

2-(*p*-Methylbenzyl)-2-bromo-1-indanone (VIII). Bromination of VII and recrystallization of the product from aqueous methanol gave white crystals: mp 127–128°; in $CCl_4$, $\nu_{C=O}$ 1726 (s), $\nu_{Ar}$ 1614 (s) cm$^{-1}$; $\lambda_{max}$ 300 m$\mu$ ($\epsilon$ 2740) and 257 m$\mu$ ($\epsilon$ 11,850).
*Anal.* Calcd for $C_{17}H_{15}OBr$: C, 64.77; H, 4.80; Br, 25.35. Found: C, 64.53; H, 4.66; Br, 25.43.

*trans*-2-(*p*-Chlorobenzal)-1-indanone (IX). Condensation of 1-indanone and *p*-chlorobenzaldehyde and recrystallization of the product from aqueous methanol gave white crystals: mp 175–176°; in $CCl_4$, $\nu_{C=O}$ 1698 (s), $\nu_{C=C}$ 1637 (s), $\nu_{Ar}$ 1620 (s) cm$^{-1}$; $\lambda_{max}$ 322 m$\mu$ ($\epsilon$ 35,600) and 230 m$\mu$ ($\epsilon$ 14,200).
*Anal.* Calcd for $C_{16}H_{11}OCl$: C, 75.44; H, 4.36; Cl, 13.92. Found: C, 75.69; H, 4.58; Cl, 13.75.

2-(*p*-Chlorobenzyl)-1-indanone (X). Hydrogenation of IX in dioxane and recrystallization of the product from *n*-hexane gave white crystals: mp 76–77°; in $CHCl_3$, $\nu_{C=O}$ 1709 (s), $\nu_{Ar}$ 1615 (m) cm$^{-1}$; $\lambda_{max}$ 295 m$\mu$ ($\epsilon$ 2890), 277 (2160), 244 (15,150).
*Anal.* Calcd for $C_{16}H_{13}OCl$: C, 74.84; H, 5.11; Cl, 13.81. Found: C, 74.61; H, 5.07; Cl, 13.88.

2-(*p*-Chlorobenzyl)-2-bromo-1-indanone (XI). Bromination of X and recrystallization of the product from aqueous ethanol gave

obtained by a thermistor method.[14] The ultraviolet irradiation used in the *trans* to *cis* isomerizations was provided by a B-100A Blakray source (Ultra-Violet Products, Inc.).

(23) D. N. Kevill and N. H. Cromwell, *J. Am. Chem. Soc.*, **83**, 3812 (1961).
(24) G. A. Coppens, D. N. Kevill, and N. H. Cromwell, *J. Org. Chem.*, **27**, 3299 (1962).
(25) A. Hassner and N. H. Cromwell, *J. Am. Chem. Soc.*, **80**, 893 (1958).
(26) N. H. Cromwell and R. P. Ayer, *ibid.*, **82**, 133 (1960).
(27) H. Leuchs, J. Wutke, and E. Giesler, *Ber.*, **46**, 2200 (1913).

white crystals: mp 101–102°; in CHCl₃, $\nu_{C=O}$ 1720 (s), $\nu_{Ar}$ 1614 (m) cm⁻¹; $\lambda_{max}$ 298 m$\mu$ ($\epsilon$ 2650) and 255 m$\mu$ ($\epsilon$ 13,500).

*Anal.* Calcd for C₁₆H₁₂OBrCl: C, 57.25; H, 3.61; Br + Cl, 34.37. Found: C, 57.42; H, 3.63; Br + Cl, 34.33.

*cis*-2-(*p*-Chlorobenzal)-3,3-dimethyl-1-indanone (XIIa). Condensation of 3,3-dimethyl-1-indanone[13] with *p*-chlorobenzaldehyde gave a product with mp 70–80° (probably a mixture of *cis* and *trans* isomers). Recrystallization from aqueous methanol gave yellow crystals: mp 95–96°; in CHCl₃, $\nu_{C=O}$ 1706 (s), $\nu_{Ar}$ 1614 (m) cm⁻¹; $\lambda_{max}$ 325 m$\mu$ ($\epsilon$ 22,380), 276 (sh) (8430), 233 (11,000).

*Anal.* Calcd for C₁₈H₁₅OCl: C, 76.45; H, 5.35; Cl, 12.54. Found: C, 76.67; H, 5.75; Cl, 12.78.

*trans*-2-(*p*-Chlorobenzal)-3,3-dimethyl-1-indanone (XII). Irradiation of XIIa in methanol with ultraviolet light[22] for 24 hr, followed by flash evaporation under reduced pressure, gave a product whose proton magnetic resonance spectrum indicated 56% *cis* and 44% *trans* isomers.[14,22] Recrystallization from aqueous methanol gave colorless crystals: mp 81–82°; in CCl₄, $\nu_{C=O}$ 1706 (s), $\nu_{C=C}$ 1627 (m), $\nu_{Ar}$ 1612 (m) cm⁻¹; $\lambda_{max}$ 322 m$\mu$ ($\epsilon$ 19,300), 278 (sh) (13,050), 224 (11,150).

*Anal.* Calcd for C₁₈H₁₅OCl: C, 76.45; H, 5.35; Cl, 12.54. Found: C, 76.20; H, 5.46; Cl, 12.55.

2-(*p*-Chlorobenzyl)-3,3-dimethyl-1-indanone (XIII). Hydrogenation of crude XIIa (probably mixture of *cis* and *trans* isomers) in ethyl acetate and recrystallization of the product from aqueous methanol gave white crystals: mp 60–61°; in CCl₄, $\nu_{C=O}$ 1720 (s), $\nu_{Ar}$ 1610 (w) cm⁻¹; $\lambda_{max}$ 325 m$\mu$ ($\epsilon$ 4690), 295 (4570), 243 (12,850).

*Anal.* Calcd for C₁₈H₁₇OCl: C, 75.91; H, 6.02; Cl, 12.45. Found: C, 76.05; H, 5.94; Cl, 12.36.

2-(*p*-Chlorobenzyl)-2-bromo-3,3-dimethyl-1-indanone (XIV). Bromination of XIII and recrystallization of the product from aqueous ethanol gave white crystals: mp 98–99°; in CCl₄, $\nu_{C=O}$ 1729 (s), $\nu_{Ar}$ 1609 (m) cm⁻¹; $\lambda_{max}$ 296 m$\mu$ ($\epsilon$ 3410) and 253 m$\mu$ ($\epsilon$ 12,200).

*Anal.* Calcd for C₁₈H₁₆OBrCl: C, 59.44; H, 4.44; Br + Cl, 31.72. Found: C, 59.28; H, 4.48; Br + Cl, 31.88.

2-(*p*-Nitrobenzyl)-1-indanone (XV). Although 2-(*p*-nitrobenzal)-1-indanone has previously been prepared,[28] it is of very limited solubility in most solvents and attempts to hydrogenate it to XV have not been successful. Compound XV was prepared using the method of Stork,[29] by an alkylation reaction through an enamine intermediate.

A 5.2-g (0.04 mole) sample of 1-indanone and 5.6 g (0.08 mole) of pyrrolidine were dissolved in 75 ml of toluene. Azeotropic distillation led to the collection of 1.50 ml of water after 72 hr. The solvent was reduced to about 10 ml by evaporation under reduced pressure. A 6.88-g (0.04 mole) sample of *p*-nitrobenzyl chloride in 150 ml of absolute methanol was added to the dark red toluene solution, and the mixture was refluxed and stirred for 48 hr. Water (15 ml) was added, and the resulting solution was stirred and refluxed for an additional 12 hr. Evaporation of solvent gave a dark red oil. Repeated extractions with ether gave 1.4 g (12.8% yield) of a yellow product of mp 115–116°. Recrystallization from aqueous methanol gave a slightly yellow product of unchanged melting point; in CHCl₃, $\nu_{C=O}$ 1706 (s), $\nu_{Ar}$ 1608 (m), $\nu_{NO_2}$ 1348 (s) cm⁻¹. The product was not analytically pure and gave 2.74% residue on analysis. Further purification was not attempted and 08.0 g was converted to XVI in the usual manner.[28]

2-(*p*-Nitrobenzyl)-2-bromo-1-indanone (XVI). Bromination of XV and recrystallization of the product from aqueous acetone gave white crystals: mp 170–171°; in CHCl₃, $\nu_{C=O}$ 1720 (s), $\nu_{Ar}$ 1608 (m), $\nu_{NO_2}$ 1350 (s) cm⁻¹.

*Anal.* Calcd for C₁₆H₁₂O₃NBr: C, 55.51; H, 3.49; Br, 23.08; N, 4.05. Found: C, 55.45; H, 3.48; Br, 23.12; N, 4.09.

2-(α,α-Dideuteriobenzyl)-2-bromo-3,3-dimethyl-1-indanone (IIa). This compound was prepared by a method identical with that

(28) G. A. Coppens, M. Coppens, D. N. Kevill, and N. H. Cromwell, *J. Org. Chem.*, **28**, 3267 (1963).
(29) G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Am. Chem. Soc.*, **85**, 207 (1963).

previously used for 2-(α,α-dideuteriobenzyl)-2-bromo-1-indanone,[1] but with 3,3-dimethyl-1-indanone[13] replacing 1-indanone and the product recrystallized from aqueous ethanol, mp 74.5–75°. The proton magnetic resonance spectrum showed the six methyl protons as a doublet at $\tau$ 8.59 ($J$ = 2.0 cps), a signal from the aromatic proton $\beta$ to the carbonyl at $\tau$ 2.25 ($J$ = 7.0 cps), and eight aromatic protons from $\tau$ 2.4 to 2.9. Especially significant is the absence of any signal in the region of $\tau$ 6.62, where the signal from the benzylic methylene protons ($J$ = 15.0 cps) occurs for 2-benzyl-2-bromo-3,3-dimethyl-1-indanone (II).

*trans* to *cis* Isomerization. Analytical samples of *cis*-exocyclic α,β-unsaturated ketones were obtained from the corresponding *trans* isomers in the manner previously described,[14] *i.e.*, by ultraviolet irradiation[22] of methanol or dioxane solutions followed by column chromatography. By this procedure, pure samples of the *cis* isomers of III, VI, and IX (IIIa, VIa, and IXa) were obtained.

*cis*-2-(*p*-Methoxybenzal)-1-indanone (IIIa) was obtained as bright yellow crystals: mp 92–93°; in CHCl₃, $\nu_{C=O}$ 1692 (s), $\nu_{Ar}$ 1612 (s) cm⁻¹.

*Anal.* Calcd for C₁₇H₁₄O₂: C, 81.55; H, 5.64; mol wt, 250. Found: C, 81.58; H, 5.60; mol wt, 252.

*cis*-2-(*p*-Methylbenzal)-1-indanone (VIa) was obtained as bright yellow crystals: mp 87–88°; in CCl₄, $\nu_{C=O}$ 1693 (s), $\nu_{Ar}$ 1612 (s) cm⁻¹; $\lambda_{max}$ 334 m$\mu$ ($\epsilon$ 21,300), 275 (sh) (7300), 232 (10,300).

*Anal.* Calcd for C₁₇H₁₄O: C, 87.15; H, 6.02. Found: C, 87.01; H, 6.25.

*cis*-2-(*p*-Chlorobenzal)-1-indanone (IXa) was formed as bright yellow crystals: mp 133–134°; in CHCl₃, $\nu_{C=O}$ 1689 (s), $\nu_{Ar}$ 1618 (s) cm⁻¹; $\lambda_{max}$ 321 m$\mu$ ($\epsilon$ 35,900) and 228 m$\mu$ ($\epsilon$ 16,800).

*Anal.* Calcd for C₁₆H₁₁OCl: C, 75.44; H, 4.36; Cl, 13.92; mol wt, 255. Found: C, 75.61; H, 4.29; Cl, 14.00; mol wt, 260.

**Kinetic Methods.** All runs were carried out using accurately measured aliquots of about 5 ml in volume; the sealed bulb technique was employed. Kinetic techniques and illustrative runs for closely related systems have been described previously.[1,4b,23]

**Product Studies.** (A) **With Halide Ion.** All the α-bromoindanones used in this investigation were allowed to react with tetraethylammonium bromide and with tetraethylammonium chloride for extended periods of time under the conditions used for kinetic measurements. Evaporation to dryness under reduced pressure, washing the residue with distilled water, filtering, and drying gave 90–97% yields of the corresponding exocyclic, α,β-unsaturated ketones. Identification was based on melting point, mixture melting point, and infrared and proton magnetic resonance spectra.

(B) **With Piperidine.** A 0.27-g sample of 2-(*p*-methoxybenzyl)-2-bromo-1-indanone (V) was heated at 74° for a period of 3 days with 0.86 g of piperidine in 25 ml of acetonitrile. The solvent was evaporated under reduced pressure, and the product was washed with water and dried. The proton magnetic resonance spectrum indicated the product to contain 85–90% *trans*-2-(*p*-methoxybenzal)-1-indanone (III) and 10–15% of 3-piperidino-2-(*p*-methoxybenzyl)-1-indanone.

Essentially identical results were obtained with 2-(*p*-chlorobenzyl)-2-bromo-1-indanone (XI) and with 2-benzyl-2-bromo-1-indanone (I).[1] 2-Benzyl-2-bromo-3,3-dimethyl-1-indanone (II), where endocyclic elimination–addition is impossible, gave a 94% yield of 2-benzal-3,3-dimethyl-1-indanone.

(C) **With Morpholine.** A 0.17-g sample of 2-(*p*-methoxybenzyl)-2-bromo-1-indanone (V) was heated at 75° for 4 days with 1.00 g of morpholine in 25 ml of acetonitrile. The solvent was removed by evaporation under reduced pressure and the product washed well with water and dried. The proton magnetic resonance spectrum was identical with that for an authentic sample of *trans*-2-(*p*-methoxybenzal)-1-indanone (III); in particular, no signals attributable to the methylene hydrogens of a morpholino substituent were observed.

Both 2-(*p*-chlorobenzyl)-2-bromo-1-indanone (XI) and 2-benzyl-2-bromo-1-indanone (I) gave identical results. Substitution of *t*-butylamine for morpholine also lead to only the appropriate exocyclic, α,β-unsaturated ketone.