[CONTRIBUTION FROM AVERY LABORATORY, UNIVERSITY OF NEBRASKA]

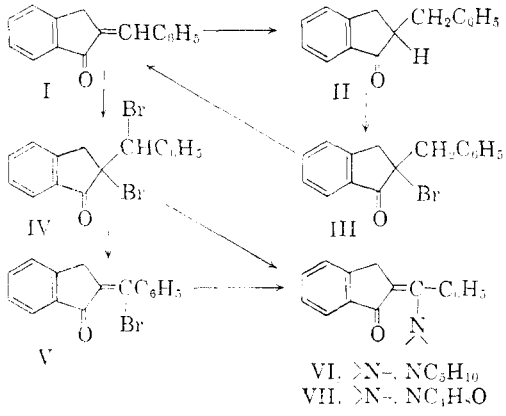
Elimination Reactions of α-Halogenated Ketones. II.[1] Reactions of 2-Bromo-2-benzyl- and 2-Bromo-2-(α-bromobenzyl)-1-indanone

BY NORMAN H. CROMWELL AND RANDALL P. AYER

RECEIVED MAY 14, 1959

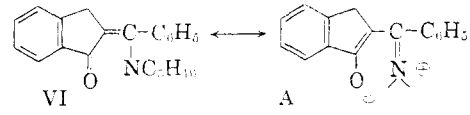
2-Bromo-2-(α-bromobenzyl)-1-indanone reacts with piperidine and morpholine to give 2-(α-piperidinobenzal)-1-indanone and 2-(α-morpholinobenzal)-1-indanone, respectively. The former product is also obtained from 2-(α-bromobenzal)-1-indanone which is produced by a thermal dehydrobromination of the dibromo ketone. The dehydrobromination of 2-bromo-2-benzyl-1-indanone with silver nitrate, sodium methoxide or amines (piperidine or γ-picoline) results in 2-benzal-1-indanone. This exocyclic elimination of hydrogen bromide from the 2-bromo-2-benzyl-1-indanones is contrasted with the endocyclic orientation of elimination previously reported[1] for the analogous 2-bromo-2-benzyl-1-tetralones. Differences in steric factors in these two systems are discussed in connection with the orientation and relative rates of elimination. A novel reaction between 2-benzoyl-1-indanone and amines has been shown to involve cleavage of the five-membered ring to produce the amides of 3-(*o*-carboxyphenyl)-propiophenone.

Several papers[1,2] have dealt with the elimination of hydrogen bromide from 2-bromo-2-benzyl-1-tetralones. It was reported that endocyclic elimination was the major reaction producing 2-benzyl-1-keto-1,4-dihydronaphthalenes as the primary products. It seemed of interest to study the elimination of hydrogen bromide from the related 2-bromo-2-benzyl-1-indanones, which, for reasons of steric differences, might be expected to give mainly exocyclic elimination to produce 2-benzal-1-indanones. This has been found to be the case.



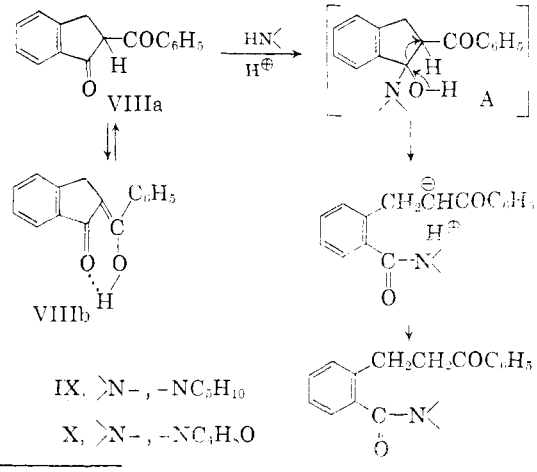
2-Bromo-2-(α-bromobenzyl)-1-indanone (IV) reacted with piperidine and morpholine to give the β-amino-α,β-unsaturated ketones VI and VII, respectively. The thermal elimination of hydrogen bromide from IV gave the β-bromo-α,β-unsaturated ketone V, which on treatment with piperidine also produced VI. The assignment of structures to V, VI and VII is based upon their elementary composition and a comparison of their ultraviolet and infrared absorption spectra with those of known compounds. These three new compounds all have strong ultraviolet maxima near 232 and 324 mμ. 2-Benzal-1-indanone shows maxima at 228 and 319 mμ (ε 9650 and 28,500).[2b] 2-Benzyl-1-indone is apparently unknown but it might be expected to show absorption of ultraviolet light similar to that of 2-ethyl-1-indone which has been reported to have maxima at 236 and 242 mμ (ε 21,800, 25,300).[3]

The introduction of a morpholino group into the β-position of chalcone causes a more pronounced bathochromic shift of the long wave length band (cinnamoyl band).[4] The ultraviolet spectrum of the hydrochloride of VI showed a small hypsochromic shift to 320 mμ (with a decrease in ε) for the long wave length band. This is to be expected if the following resonance (VI⟷A) makes a contribution to the excited state of VI.



The infrared carbonyl stretching vibrations for the 2-benzal-1-indanones I, V, VI and VII were located between 1704 and 1710 cm.$^{-1}$, and the strong characteristic Ar C=C bands were found between 1630 and 1633 cm.$^{-1}$ which are absent in the infrared spectra of indones.[3]

Attempts to hydrolyze the β-amino-α,β-unsaturated ketone VI to 2-benzoyl-1-indanone (VIII) using acid conditions were not successful. The reaction of 2-benzoyl-1-indanone (VIII) with piperidine and with morpholine gave a novel reaction involving a cleavage of the five-membered ring. The structures of the resulting amide



(1) For paper I, see N. H. Cromwell, R. P. Ayer and P. W. Foster, THIS JOURNAL, **82**, 130 (1960).

(2) (a) A. Hassner, N. H. Cromwell and S. J. Davis, *ibid.*, **79**, 230 (1957); (b) A. Hassner and N. H. Cromwell, *ibid.*, **80**, 893 (1958); (c) **80**, 901 (1958).

(3) H. O. House and D. J. Reif, *ibid.*, **79**, 6491 (1957). In a private communication, Dr. House reports that 2-bromo-2-ethylindanone reacts with collidine to give a 20% yield of 2-ethylindone and an 80% yield of 2-ethylidineindanone which shows λ_{max} (ethanol) 266 mμ (ε 22,600); $\gamma_{C=O}$, 1710 cm.$^{-1}$ and $\gamma_{C=C}$, 1660 cm.$^{-1}$ (CCl_4).

(4) See N. H. Cromwell and W. R. Watson, *J. Org. Chem.*, **14**, 411 (1949),

derivatives IX and X of the 3-(*o*-carboxyphenyl)-propiophenone were readily established by absorption spectra studies. Hauser has reported that sodium hydroxide reacts with 2-benzoyl-1-indanone (VIII)[5] to give mainly 1-indanone and benzoic acid, but he also obtained a small amount of material of m.p. 88–89°, which they thought was probably 3-(*o*-carboxyphenyl)-propiophenone.

The infrared spectrum of 2-benzoyl-1-indanone shows a five-membered ring carbonyl band at 1715 cm.$^{-1}$ and a broad conjugated, chelated carbonyl band from 1700–1500 cm.$^{-1}$. The ultraviolet spectrum of this 1,3-diketone shows maxima at 248 and 350 mμ. The structure of this compound is probably best given by VIIIb, but the amines probably react with the VIIIa tautomer to form IX and X.

The fact that 2-(α-piperidinobenzal)-1-indanone (VI) is obtained starting with either the dibromoketone IV or the very reactive β-bromo-α,β-unsaturated ketone V suggests that the first step in the reaction of IV with amines may be the exocyclic loss of hydrogen bromide to produce V. It previously had been shown[2c] that the analogous 2-bromo-2-(α-bromobenzyl)-4,4-dimethyl-1-tetralone loses a molecule of hydrogen bromide to introduce an endocyclic double bond on heating, and presumably on treatment with amines. It was also established[1,2c] that 2-bromo-2-benzyl-4,4-dimethyl-1-tetralone reacts with various reagents to give endocyclic elimination. It therefore seemed of importance to study the elimination of hydrogen bromide from the related 2-bromo-2-benzyl-1-indanone (III).

2-Benzyl-1-indanone (II) was prepared by the catalytic hydrogenation of (I) in the presence of palladium-on-charcoal. Attempts to carry out this hydrogenation using platinum oxide catalyst did not give good yields of the desired product II. Instead considerable amounts of a colorless solid, m.p. 90–94°, resulted which infrared spectra studies indicated had a carbonyl band at 1711 cm.$^{-1}$ and an hydroxyl band at 3575 cm.$^{-1}$. Phillips[6] apparently encountered a similar difficulty with the attempt to hydrogenate 2-benzal-1-pentanone in the presence of a platinum catalyst. The ketone II was readily brominated to produce the desired 2-bromo-2-benzyl-1-indanone (III) for the dehydrohalogenation studies.

A comparison of the infrared carbonyl stretching frequency of the bromoketone III with that of the parent ketone II shows an increase in frequency of 11 cm.$^{-1}$. The magnitude of this shift is about what would be expected if the benzyl and bromine groups are symmetrically arranged at the 2-position with respect to the plane of the five-membered ring and to the carbonyl group and are thus eclipsed with the hydrogens at the 3-positions. An equatorial conformation for the bromine would be expected to produce a shift of 20–22 cm.$^{-1}$ while an axial arrangement should give almost no change.[2b]

Treatment of the bromoketone III with silver nitrate, piperidine, γ-picoline or sodium methoxide produced as the isolable product 2-benzal-1-indanone (I), identical in all respects with the compound obtained by the base-catalyzed condensation of benzaldehyde with 1-indanone.[2b]

The fact that the reaction of III with silver nitrate is much slower than the corresponding reaction with 2-bromo-2-benzyl-4,4-dimethyl-1-tetralone[1] clearly indicates that the bromine in III is much less readily ionized than that in the tetralone compound. The reasons for this considerable difference in reactivity may not be clear until the definitive rate studies now being carried out with various α-halo ketones are complete. Nevertheless, the following comparative structural factors can be mentioned at this time. It has been suggested that the ionization of bromine in 2-bromo-2-benzyl-4,4-dimethyl-1-tetralone receives some endocyclic C_β–H bond electron assistance.[1] Since the two hydrogen atoms on the endocyclic β-position are eclipsed with the bromine and benzyl groups in III, such C_β–H bond electron assistance for the ionization of bromine is not to be expected in this case. It is also possible that the transition state for the carbonium ion is less readily attained in the more rigid structure III than is the case with the more flexible 2-benzyl-2-bromo-1-tetralones.

These preliminary product studies of the elimination of hydrogen bromide from III using amines (piperidine and γ-picoline) indicated that reaction was at least as fast or possibly a bit faster than was the case with the analogous 2-bromo-2-benzyl-4,4-dimethyl-1-tetralone.[2c,7] Although preliminary kinetic studies[7] have indicated that piperidine reacts with III by a mechanism showing second-order kinetics, some related studies with β-deuterated analogs of III are necessary to establish whether or not this exocyclic elimination is a typical E2 type, a non-concerted carbanion reaction[8] or involves an SN2 type of transition state which collapses to give the elimination instead of a substitution product.[2]

The exocyclic α,β-unsaturated ketone I may be the favored isomer both kinetically and thermodynamically. Attempts to rearrange 2-benzal-1-indanone to the unknown 2-benzyl-1-indone by heating with palladium[1] were not successful. Whatever may be the mechanism of elimination of hydrogen bromide under these various conditions, a facile endocyclic 2,3-diaxial loss of hydrogen bromide to give 2-benzyl-1-indone might not be expected because of the eclipsed arrangement of the groups in the 2- and 3-positions of the five-membered ring.[9]

Acknowledgment.—This work was supported in part by grant No. CY2931, National Cancer Institute, U. S. Public Health Service, and by the John Simon Guggenheim Memorial Foundation to whom the senior author is indebted for a fellow-

(5) C. R. Hauser, F. W. Swamer and B. I. Ringler, THIS JOURNAL, **70**, 4023 (1948).

(6) A. P. Phillips and J. Mentha, *ibid.*, **78**, 140 (1956).

(7) In some unpublished work R. P. Ayer has now found that the reaction of 2-bromo-2-benzyl-1-indanone with piperidine in benzene shows second-order kinetics and is twice as fast as the corresponding second-order reaction of 2-bromo-2-benzyl-4,4-dimethyl-1-tetralone at 60° and at 90°.

(8) V. J. Shiner and M. L. Smith, THIS JOURNAL, **80**, 4095 (1958).

(9) J. Weinstock, R. G. Pearson and F. G. Bordwell, *ibid.*, **78**, 3468, 3473 (1956), have shown that a *trans* elimination is favored even in a cyclopentane ring. It is possible that the extra rigidity of the five-ring structure in the indanones is less favorable for an endocyclic elimination of *trans* arranged groups.

ship in 1958. The helpful suggestions of Dr. Y. Pocker of the Chemistry Department, University College, London, are gratefully acknowledged.

Experimental[10]

2-Benzyl-1-indanone (II).—A 4.0-g. (0.018 mole) sample of 2-benzal-1-indanone (I)[2b] in 150 ml. of methanol was shaken with hydrogen at one atmosphere of pressure in a quantitative hydrogenator in the presence of 0.06 g. of 10% palladium-on-charcoal catalyst. One mole of hydrogen was consumed in 2 hours. Removal of the catalyst and distillation of the product gave 3.22 g. (80.5% yield) of a colorless viscous liquid, b.p. 160–164° (1.75 mm.), $n^{25}D$ 1.5954 (lit.[11] b.p. 222° (18 mm.); λ_{max} 245, 270, (291) mμ (ε 12,620, 1105, 2395); γ C = O, 1717 cm.$^{-1}$.

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.16; H, 6.64.

2-Bromo-2-benzyl-1-indanone (III) was obtained in 81% yield by the method of Leuchs,[12] m.p. 80–81°, recrystallized from 95% ethanol; λ_{max} 257, (291), mμ (ε 12,600, 3,200); γC = O, 1728 cm.$^{-1}$.

2-Bromo-2-(α-bromobenzyl)-1-indanone (IV).—A 2.5-g. (0.0144 mole) sample of 2-benzal-1-indanone (I)[2b] was treated with 1.82 g. (0.0144 mole) of bromine in 25 ml. of carbon tetrachloride in the absence of light to produce 3.5 g. (81% yield) of a colorless solid, m.p. 144–145°, recrystallized from benzene and petroleum ether (b.p. 88–98°)[13]; λ_{max} 257, (295) mμ (ε 14,400, 2,600); γC=O, 1736 cm.$^{-1}$.

2-(α-Bromobenzal)-1-indanone (V).—A 1.0-g. (0.00263 mole) sample of the dibromo-ketone IV was slowly heated in a side arm testtube through which nitrogen was passed. On melting, the dibromide bubbled as it eliminated hydrogen bromide. The temperature of the oil-bath was held at 160° until the evolution of gas ceased. The residue was taken up in diisopropyl ether and washed with water. Evaporation of the solvent and recrystallization of the residue from petroleum ether (b.p 60–70°) gave colorless crystals, 0.51 g. (65% yield), m.p. 116.5–118°; λ_{max} 232, 325 mμ (ε 14,600, 23,900); γC=O 1710 cm.$^{-1}$; γAr C=C, 1630 cm.$^{-1}$. This compound gave an immediate precipitate with alcoholic silver nitrate.

Anal. Calcd. for $C_{16}H_{11}OBr$: C, 64.23; H, 3.71; Br, 26.71. Found: C, 64.34; H, 3.83; Br, 26.65.

2-(α-Piperidinobenzal)-1-indanone (VI). (a) From the Dibromoketone IV.—A 2.5-g. (0.0066 mole) sample of the dibromoketone IV and 5.8 g. (0.066 mole) of piperidine were dissolved in 50 ml. of benzene and allowed to stand at room temperature for 16 hours to produce a 93% yield of piperidine hydrobromide and a 70% yield of the yellow colored amino-unsaturated ketone VI, m.p. 142–143°, recrystallized from 95% ethanol; λ_{max} 232, 324 mμ (ε 13,100, 24,000); γC=O, 1704 cm.$^{-1}$ (1697 cm.$^{-1}$, Nujol); γAr C=C, 1633 cm.$^{-1}$ (1628 cm.$^{-1}$ Nujol).

(b) From the β-Bromo-α,β-unsaturated Ketone V.—A 0.5-g. (0.00167 mole) sample of V and 1.42 g. (0.0167 mole) of piperidine were dissolved in 10 ml. of benzene. After standing at room temperature for 17 hours in a nitrogen atmosphere diisopropyl ether was added and the piperidine hydrobromide removed by filtration; 0.28 g. (100% yield). Evaporation of the solvent left a yellow colored solid which was recrystallized from 95% ethanol to give 0.38 g. (75% yield) of yellow colored crystals, m.p. 142–143°, identical with the product VI obtained by the method (a).

Anal. Calcd. for $C_{21}H_{21}ON$: C, 83.13; H, 6.98; N, 4.62. Found: C, 83.23; H, 6.89; N, 4.83.

The hydrochloride of VI, m.p. 162–163°, recrystallized from abs. ethanol and ether, was obtained by treating an ether solution of VI with dry hydrogen chloride; λ_{max} 230, 320 mμ (ε 12,300, 21,200); γC=O, 1709 cm.$^{-1}$; γArC=C, 1630 cm.$^{-1}$ (Nujol).

Anal. Calcd. for $C_{21}H_{22}ONCl$: C, 74.21; H, 6.52; N, 4.12. Found: C, 74.06; H, 6.72; N, 4.08.

Attempted Hydrolysis of VI.—After refluxing with 20% sulfuric acid for 24 hours, 33% of a sample of VI was recovered. Traces of benzaldehyde were present in the reaction mixture but no other material was identified.

2-(α-Morpholinobenzal)-1-indanone (VII).—A 2.5-g. (0.00658 mole) sample of the dibromoketone IV was dissolved in 5.75 g. (0.0658 mole) of morpholine and allowed to stand in a nitrogen atmosphere for 22 hours at room temperature. Isopropyl ether was added to precipitate 2.0 g. (91% yield) of morpholine hydrobromide. From the filtrate was obtained 0.55 g. (25% yield) of a yellow crystalline product, m.p. 138–139.5°, recrystallized from 95% ethanol; λ_{max} 231, 323 mμ (ε 12,400, 24,200); γC=O, 1705 cm.$^{-1}$, γAr C=C, 1633 cm.$^{-1}$. Indications are that amines also cause some debromination of IV to produce 2-benzal-1-indanone (I).

Anal. Calcd. for $C_{20}H_{19}O_2N$: C, 78.66; H, 6.27; N, 4.59. Found: C, 78.76; H, 6.43; N, 4.82.

Dehydrobromination of 2-Bromo-2-benzyl-1-indanone (III). (a) With Silver Nitrate.—A 0.5-g. (0.00166 mole) sample of III was warmed for 4 hours at 78° and then allowed to stand in the absence of light at room temperature for 5.5 days with 0.29 g. (0.00170 mole) of silver nitrate in 2.5 ml. of ethanol and 1 ml. of water. After this treatment 0.10 g. (32% yield) of silver bromide was formed. After adding several more molar equivalents of silver nitrate over a period of 15 days a 92% yield of silver bromide resulted and from the filtrate was isolated 0.22 g. (60% yield) of 2-benzal-1-indanone (I), m.p. 109.5–111.5°.[2b]

(b) With Piperidine.—A 1.0-g. (0.00332 mole) sample of III was allowed to stand for 48 hours in 4 ml. of benzene containing 0.847 g. (0.00996 mole) of piperidine at room temperature to give 0.55 g. (100% yield) of piperidine hydrobromide and 0.48 g. (66% yield) of 2-benzal-1-indanone (I).

(c) With γ-Picoline.—A 0.5-g. (0.00166 mole) sample of III on standing at room temperature for 48 hours with 1.24 g. (0.01328 mole) of γ-picoline produced 0.094 g. (32% yield) of γ-picoline hydrobromide. Heating a sample of III in benzene with 8 molar equivalents of γ-picoline at 70° for 6.5 hours gave a 33% yield of the salt and a 30% yield of the unsaturated ketone I.

(d) With Sodium Methoxide.—A 1.0-g. (0.00332 mole) sample of the α-bromo-ketone III was dissolved in a solution of 1.96 g. (0.0166 mole) of sodium methoxide in 275 ml. of dry methanol. After standing in the dark at room temperature for 7 days the reaction mixture was made slightly acidic with gl. acetic acid and evaporated under vacuum to give a yellow colored residue. Recrystallization of this product from ethanol gave 0.22 g. (30% yield) of pure 2-benzal-1-indanone, m.p. 110–111°.

(e) Heating in Dry Benzene.—Heating a sample of the α-bromoketone III in dry benzene in a sealed tube at 105° for 18 hours gave no change as shown by evaporation of the solvent and a determination of the infrared spectrum of the residual material.

Attempted Rearrangement of 2-Benzal-1-indanone (I) to 2-Benzyl-1-indone.—When 1.0 g. of 2-benzal-1-indanone was refluxed for 2 hours in 10 ml. of ethylene glycol containing 0.1 g. of 10% palladium-on-charcoal, 0.99 g. of the starting material was recovered.

2-Benzoyl-1-indanone (VIII) was prepared by a modification of the procedure of Hauser[5] and co-workers using benzene in place of ether and refluxing 5.9 g. (0.15) mole) of sodium amide, 5.0 g. (0.038 mole) of indanone and 7.9 g. (0.04 mole) of phenyl benzoate for two hours with stirring. A 58% yield of product, m.p. 100°, resulted; λ_{max} 248 and 350 mμ (ε 11,400 and 18,700); γC=O, 1716 cm.$^{-1}$ and a broad band from 1700–1500 cm.$^{-1}$, typical of chelated, enolized 1,3-diketones.[14] This compound VIII gives a dark green color with alcoholic ferric chloride.

Reactions of 2-Benzoyl-1-indanone (VIII) with Amines. (a) With Piperidine.—A 1.0-g. (0.00425 mole) amount of VIII was dissolved in 1.81 g. (0.0213 mole) of piperidine, one drop of concd. hydrochloric acid added, and the solution refluxed for 8 hours. After standing at room temperature for 16 hours diisopropyl ether was added and the solution washed free of piperidine with water. Evaporation of the solvent and recrystallization of the residue from ethanol

(10) Melting points were read with a calibrated thermometer. Ultraviolet absorption spectra were determined with a Cary model 11-MS recording spectrophotometer using reagent grade methanol solutions. Infrared spectra were measured with a Perkin-Elmer model 21 double beam recording instrument employing sodium chloride optics and matched sodium chloride cells with CCl_4 solutions, unless otherwise indicated.

(11) W. H. Mills and A. T. Akers, *J. Chem. Soc.*, **127**, 2476 (1925).

(12) H. Leuchs, J. Wutke and E. Gieseler, *Ber.*, **46**, 2200 (1913).

(13) F. S. Kipping, *J. Chem. Soc.*, **65**, 480 (1894).

(14) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 2nd edition, 1958, p. 142.

gave a colorless product, IX, wt. 1.01 g. (79% yield), m.p. 90–91°, λ_{max} (benzoyl band) 242 mμ (ε 15,600); γbenzoyl C=O, 1690 cm.$^{-1}$/86; γamide C=O, 1635 cm.$^{-1}$/96; γphenyl, 1603 cm.$^{-1}$/48.

Anal. Calcd. for $C_{21}H_{23}NO_2$: C, 78.47; H, 7.21; N, 4.36. Found: C, 78.38; H, 7.14; N, 4.23.

(b) With Morpholine.—An experiment employing morpholine in place of piperidine, as described in (a), produced 0.4 g. of X, m.p. 132–133°, λ_{max} (benzoyl band) 240 mμ (ε 15,500); γbenzoyl C=O, 1690 cm.$^{-1}$/86; γamide C=O, 1643 cm.$^{-1}$/98; γAr, 1604 cm.$^{-1}$/52.

Anal. Calcd. for $C_{20}H_{21}NO_3$: C, 74.28; H, 6.55; N, 4.33. Found: C, 74.37; H, 6.57; N, 4.10.

Both IX and X were soluble in ether, insoluble in water or dil. hydrochloric acid, and neither gave a color change with alcoholic ferric chloride solution.

LINCOLN, NEBR.

[CONTRIBUTION FROM AVERY LABORATORY, UNIVERSITY OF NEBRASKA]

Elimination Reactions of α-Halogenated Ketones. III.[1] Dehydrobromination of 4-Biphenylyl 1-Bromocyclohexyl Ketone

BY NORMAN H. CROMWELL AND PATRICK H. HESS

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The α-bromoketone, 4-biphenylyl 1-bromocyclohexyl ketone (II), was synthesized and its reactivity with secondary and tertiary amines investigated. These reactions gave only dehydrobromination with no substitution or rearrangement products being found. On the other hand, silver nitrate was found to react with II in the expected manner to give some of the Faworskii rearrangement product, 1-(4-biphenylyl)-cyclohexanecarboxylic acid, along with larger amounts of the α,β-unsaturated ketone, 4-biphenylyl 1-cyclohexenyl ketone (III). A preliminary discussion of possible factors including Cβ-H participation, responsible for the facile elimination of hydrogen bromide from this tertiary alicyclic α-haloketone is given.

Previous investigations[1,2] have shown that the alicyclic α-bromoketones 2-bromo-2-benzyl-1-tetralones[2] and 2-bromo-2-benzyl-1-indanones[1] are readily dehydrobrominated by amines and various other reagents such as alcoholic sodium hydroxide, sodium methoxide, silver nitrate, etc., to give good yields of α,β-unsaturated ketones.

Several other groups of investigators[3] have reported on studies of the reactions of various types of tertiary α-haloketones with strong bases and with alcoholic silver nitrate. These reactions have been found to lead to a variety of products including epoxy ethers,[3d] substitution products,[3e] α,β-unsaturated ketones[3a,3e] and Faworskii rearrangement products (*e.g.*, carboxylic acids),[3a–d] depending on the structure of the α-haloketone and the conditions of the reaction.

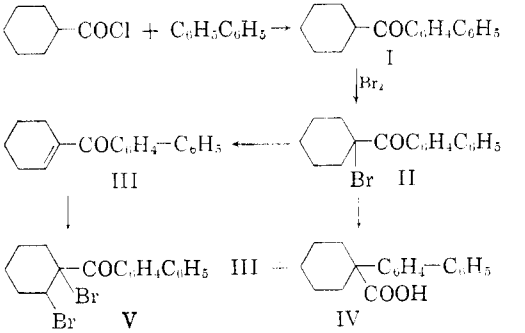
Stevens and Farkas[3e] reported that α-chlorocyclohexyl phenyl ketone reacts with alcoholic silver nitrate to produce an 18% yield of 1-phenylcyclohexanecarboxylic acid and also obtained evidence for the presence of a 68% yield of 1-cyclohexenyl phenyl ketone.

Our current major interest in the reactions of such α-haloketones is concerned with the structural factors and conditions which favor the elimination reaction to produce α,β-unsaturated ketones. We hope to be able to establish the mechanisms of these elimination reactions.

To learn whether amines would give the elimination, substitution or rearrangement reactions with tertiary α-haloketones of the α-halocyclohexyl aryl ketone type, as studied by Stevens and Farkas,[3d–e] we synthesized 4-biphenylyl cyclohexyl ketone (I) by a Friedel–Crafts synthesis with cyclohexanecarbonyl chloride and biphenyl and then brominated it to produce 4-biphenylyl 1-bromocyclohexyl ketone (II).

The practical dehydrobromination of II to produce the α,β-unsaturated ketone, 4-biphenylyl 1-cyclohexenyl ketone (III), was readily accomplished by heating with 4-picoline at 80–90° for two hours. At room temperature 4-picoline gave no measurable amount of reaction with II in four hours. The stronger secondary amines, morpholine and piperidine, also produced the unsaturated ketone III in good yields even at a room temperature, with no trace of a substitution, rearrangement or addition product being found.

A comparative product study with 4-picoline, 3-picoline and γ-collidine at about 80° showed no appreciable difference for the first two bases in their ability to eliminate hydrogen bromide from this alicyclic tertiary α-haloketone II; both gave a 93% reaction in 2.25 hours. Under these conditions the sterically hindered γ-collidine gave only an 8.5% reaction.



It appears that the elimination of hydrogen bromide from the cyclic α-bromoketone II is sensitive to both the basic strength and the steric

(1) For the previous paper in this series see, N. H. Cromwell and R. P. Ayer, THIS JOURNAL, **81**, 133 (1959).

(2) (a) A. Hassner and N. H. Cromwell, *ibid.*, **80**, 901 (1958); (b) N. H. Cromwell, R. P. Ayer and P. W. Foster, *ibid.*, **81**, 130 (1959).

(3) (a) B. Tchoubar and O. Sackur, *Compt. rend.*, **205**, 1020 (1939); (b) A. C. Cope and E. S. Graham, THIS JOURNAL, **73**, 4702 (1951); (c) R. B. Loftfield, *ibid.*, **73**, 4707 (1951); (d) C. L. Stevens and E. Farkas, *ibid.*, **74**, 618 (1952); (e) **74**, 5352 (1952).