lowered the conversion of 1-bromoadamantane to 1-chloroadamantane.

**Halogen Exchange with Mercuric Chloride.** A mixture of 29 mg (0.133 mmol) of 1-bromoadamantane and 43 mg (0.2 mmol) of mercuric chloride in 20 ml of carbon tetrachloride was heated at 60° for 3 hr in a sealed tube. The usual work-up and analysis showed that the yield of 1-chloroadamantane was 95%. When silver chloride was used in place of mercuric chloride, the conversion of 1-bromoadamantane to 1-chloroadamantane was somewhat lowered.

# Zwitter Annihilation in the Halogenation of Allylic Alkoxides. The $\Delta^8$-1-Phenyl-1-octalol System[1]

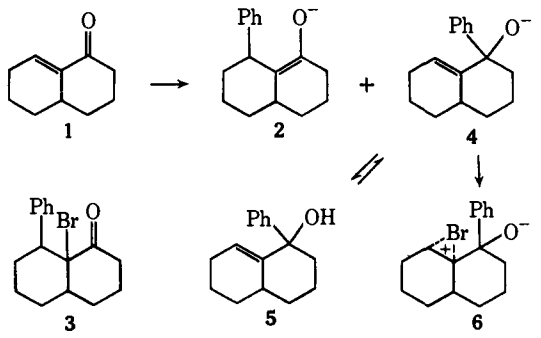
**Hugh W. Thompson* and Richard R. Muccino[2]**

*Contribution from the Department of Chemistry, Rutgers University, Newark, New Jersey 07102.* *Received April 23, 1971*

**Abstract:** Treatment of the magnesium bromide salt of $\Delta^8$-1-phenyl-1-octalol (**4a**) with bromine leads to two rearranged $\beta$-bromo ketones **10b** and **11b**, whose carbon skeletons and stereochemistry have been established by independent syntheses. It is shown that for at least one of the products, rearrangement results from collapse of a bromonium alkoxide intermediate in the halogenation. This interpretation is discussed in terms of related rearrangement mechanisms and homoenolate structures.

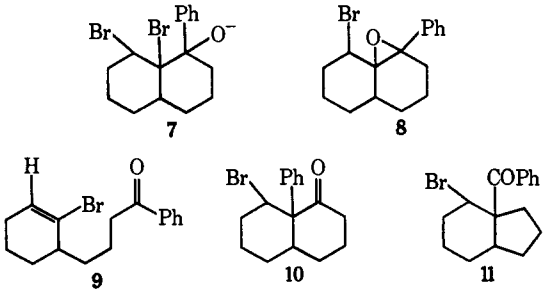
In the course of other synthetic work we required a method for preparing bromo ketone **3**, and consequently attempted direct halogenation of the magnesium enolate **2**, obtained by conjugate addition of phenyl Grignard to $\Delta^8$-1-octalone (**1**).[3] We isolated, in addition to an $\alpha$-bromo ketone,[3] an isomeric monobromo ketone, mp 110–112.5°,[3] whose spectral and chemical properties, however, could not all be reconciled with a structure bearing the halogen at a position $\alpha$ to the carbonyl group.[4,5]

Scheme I



At this juncture, we perceived that bromination of the "normal" Grignard product known to be present in the mixture,[3] a tertiary allylic alkoxide **4**, might, by internal neutralization of the intermediate **6**, give rise to ketonic products bearing bromine at sites more remote from the carbonyl group than we had originally anticipated.

This presumed intermediate in the bromination of **4**, the bromonium alkoxide **6**, could theoretically undergo a variety of reactions. The simplest of these would be attack by bromide ion to give a dibromo alkoxide (**7**), or direct internal attack of the alkoxide at either the more positive or more accessible of the two carbon atoms involved in the bromonium ion, to give a bromo epoxide **8** (or an oxetane). If the zwitter annihilation were not to take place by direct attack of the alkoxide on the bromonium ion, the presence of a tetrahedral carbon between the positively and negatively charged centers would require migration of one of the tetrahedral bonds to allow neutralization. Three different simple rearrangment products are possible, **9**–**11**, each corresponding to migration of one of the bonds at the alkoxide carbon.



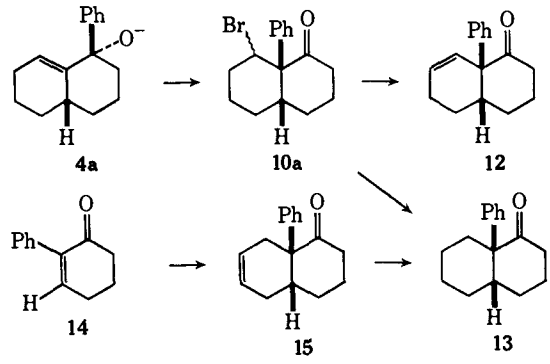
Of the three possible ketonic products, only **10** fits the infrared spectral data for our compound. The tentative conclusion that our bromo ketone was **10**, which arose from **4** present during the bromination, was therefore tested by bromination of the pure allylic alkoxide **4** and independent synthesis of the carbon skeleton of **10**. A sample of the isolated and purified tertiary alcohol **5**[3] was reconverted with phenylmagnesium bromide to its salt, **4**, and brominated. Work-up by addition of basic, saturated aqueous ammonium chloride, followed by chromatography, provided the same bromo ketone **10** in 36.5% yield.

For several reasons involving steric and electronic factors in **1**, the stereochemistry of **4** is believed to be that shown in **4a** (Scheme II).[3,6] This stereochemistry

(1) Abstracted in part from the Ph.D. Thesis of R. R. M.
(2) National Institutes of Health Predoctoral Fellow, 1970–1971.
(3) H. O. House and H. W. Thompson, *J. Org. Chem.*, **28**, 360 (1963).
(4) L. F. Fieser and M. Fieser, "Steroids," Reinhold, New York, N. Y., 1959, pp 170, 282–284.
(5) (a) A. Nickon, M. A. Castle, R. Harada, C. E. Berkoff, and R. O. Williams, *J. Amer. Chem. Soc.*, **85**, 2185 (1963); (b) A. Baretta, J. P. Zahra, B. Waegell, and C. W. Jefford, *Tetrahedron* **26**, 15 (1970).
(6) E. Toromanoff, *Top. Stereochem.*, **2**, 187 (1967).

for **4** requires that by whatever migration mechanism **10** is produced, the cis relationship should be maintained between the phenyl and the ring-juncture hydrogen (**10a**). While unambiguous independent synthesis of either epimer of this bromo ketone would certainly be difficult, its hydrogenolysis product, 9-phenyl-*cis*-1-decalone (**13**), was synthesized with relative ease as follows (Scheme II). Reaction of 2-phenylcyclohexenone (**14**) with excess butadiene in benzene at 50–60° in the presence of *ca.* 0.5 equiv of aluminum chloride afforded, among other products, **15**[7] as a crystalline solid isolable by chromatography in 28.5% yield. Catalytic hydrogenation of this material gave in 67% yield 9-phenyl-*cis*-1-decalone (**13**), identical in every respect with the hydrogenolysis product of **10**. In addition, the presence of small amounts of **13** was detected in the mixture resulting from treatment of 9-chloro-*trans*-1-decalone[8] with phenyl Grignard.[9,10]

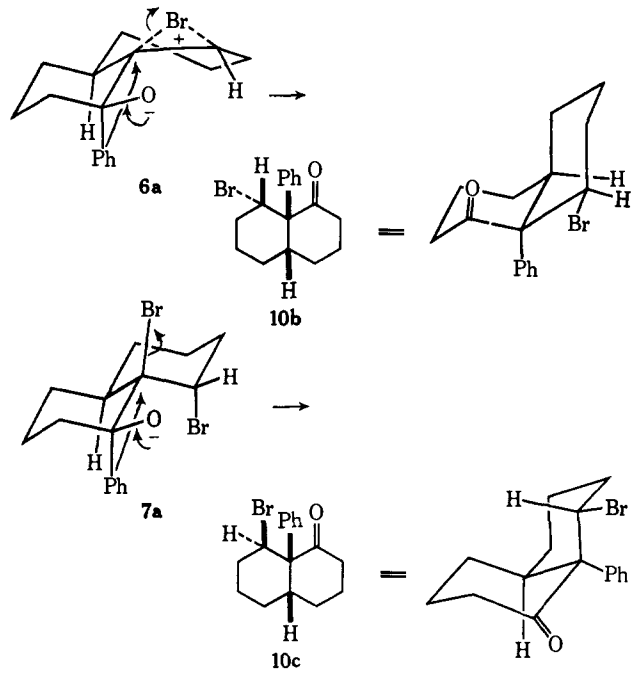
Scheme II




Although this confirms unambiguously the carbon skeleton and ring-juncture stereochemistry of **10a**, it does not specify either the position or stereochemistry of the bromine atom. Its position may be deduced from the restrictions imposed by the known structure of the starting material for this sequence, $\Delta^8$-1-octalone (**1**),[3,8] and the fact that dehydrohalogenation of **10a** gives a single, nonconjugated product with two vinyl hydrogens, which is not identical with **15**.

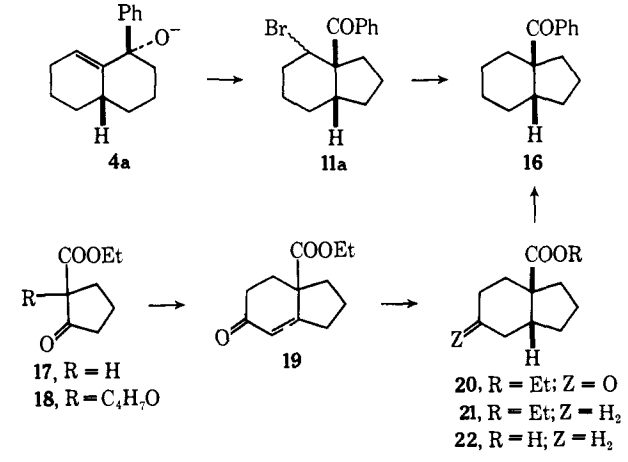
The stereochemistry shown for **4a** suggests that the side trans to the phenyl group is the less hindered and that therefore the principal bromonium ion involved should be that shown in **6a** (Scheme III). This is consistent with a cis ring juncture for **10** but plausible mechanisms can be devised to account for formation of either of the two possible epimers of **10a** (Scheme III). The spectral information clearly favors structure **10b** for the following reason. Because of axial ring interactions, the preferred conformations of **10b** and **10c** will be those shown in Scheme III (axial H, consistent with the nmr data); however, the ultraviolet spectrum of **10a** displays a ketone n → $\pi^*$ maximum at 299.5 nm, characteristic of a cyclohexanone or decalone with an axial $\alpha$ electron-withdrawing substituent.[11] Hence, we infer that the correct stereochemistry is **10b** and the mechanism of formation is **6a**.

Scheme III




Bromination of the pure allylic alkoxide **4a** provided, in addition to **10b**, 27.7% of a second, isomeric bromo ketone, mp 77–77.5°. The infrared spectrum of this material displays carbonyl absorption at 1680 $cm^{-1}$, consistent with either of the two conceivable rearrangement products **9** or **11**. However, the nmr spectrum of this compound shows absorption between $\delta$ 2.9 and 7.25 only for a 1-H quartet ($J$ = 6 and 10 Hz) centered at $\delta$ 4.85, and is therefore inconsistent with structure **9**.[12] That **11a** is the correct structure was demonstrated by catalytic hydrogenolysis and comparison of the product **16** with material synthesized by an independent route (Scheme IV).[13,14]

Scheme IV



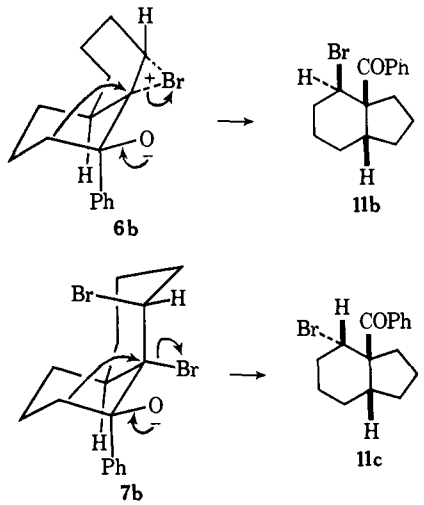

The catalytic hydrogenolysis of **10** and **11** gave materials which were in each case the more stable of two possible epimers.[15] We therefore needed to establish that

(7) H. W. Thompson and D. G. Melillo, *J. Amer. Chem. Soc.*, **92**, 3218 (1970).
(8) H. O. House and H. W. Thompson, *J. Org. Chem.*, **26**, 3729 (1961).
(9) A. S. Hussey and R. R. Herr, *ibid.*, 24, 843 (1959).
(10) A. J. Sisti and A. C. Vitale, *Tetrahedron Lett.*, 2269 (1969).
(11) (a) Reference 4, pp 175–176; (b) H. O. House and H. W. Thompson, *J. Org. Chem.*, **28**, 164 (1963), Table I; (c) R. C. Cookson and N. S. Wariyar, *J. Chem. Soc.*, 2302 (1956).
(12) (a) J. H. Richards and W. F. Beach, *J. Org. Chem.*, **26**, 623 (1961); (b) S. W. Tobey, *ibid.*, **34**, 1281 (1969).
(13) W. G. Dauben, J. W. McFarland, and J. B. Rogan, *ibid.*, **26**, 297 (1961).
(14) (a) T. M. Bare and H. O. House in *Org. Syn.*, **49**, 81 (1969); (b) M. J. Jorgenson, *Org. React.*, **18**, 1 (1970).
(15) (a) N. L. Allinger and J. L. Coke, *J. Amer. Chem. Soc.*, **81**, 4080 (1959); (b) F. Sondheimer and D. Rosenthal, *ibid.*, **80**, 3995 (1958);

**13** and **16** truly represented the stereochemistries of their precursors and did not result from ring-juncture equilibration by the relatively large quantity of catalyst used. The compound *trans*-9a-carbomethoxy-7-methoxy-2,2-ethylenedioxy-1,2,3,4,4a,9a-hexahydrofluorene, which we had available from other work, is known to be the less stable of the two possible epimers having that carbon skeleton. In addition, the potentially epimerizable 4a-hydrogen is benzylic and therefore presumably even more susceptible than the corresponding hydrogens in **10**, **11**, **13**, or **16** to epimerization. Hence, the failure of this compound to isomerize under our hydrogenolysis conditions constitutes good evidence that ring systems **13** and **16** are also stable with respect to catalytic equilibration.

Again in the case of **11a** two mechanisms would lead to bromo ketones of the correct carbon skeleton and stereochemistry, but differing in the stereochemistry of bromine (Scheme V). Present data cannot distinguish between these alternatives; however, we are inclined to favor **11b** on the grounds that, while the stereochemistry determined for **10** (**10b**) establishes that zwitter annihilation is an operative mechanism in this system, the evidence concerning magnesium salts of halohydrins generally similar to **7** indicates that they are usually stable at our temperatures (ice bath) and must be heated to induce rearrangement.[9,10,16]

**Scheme V**

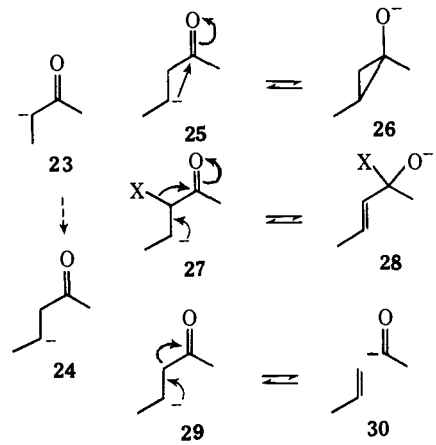



We have not been able to demonstrate the presence of any of the alternative possible products **7–9** of the bromination of **4a**. However, on the above evidence we have assigned structures **10b** and **11b** to the two materials isolated from this reaction (accounting for some 64% of the starting material). The simplest explanation for their formation is that they result from direct collapse of the zwitterions arising from bromine attachment on, respectively, the top and bottom sides of **4a**. This may be contrasted with recently reported results in the halogenation of (neutral) allylic alcohols,[17] where direct rearrangement of the intermediate halonium alcohols occurred only in solvents of high polarity. In solvents similar to ours ($Et_2O$–$CH_2Cl_2$) apparently products from simple olefin addition rather than rearrangement were observed, bearing out the logical idea that decreased electron density on oxygen retards rearrangement.

The mechanism of the rearrangement observed can be discussed from the point of view of several familiar reaction types. Since the species involved may be considered to bear at the same time both positive and negative charge, their behavior is reminiscent in part of acid-catalyzed migration from a teriary alcohol carbon, as in the pinacol rearrangement[18] and also of similar carbonyl-producing reactions which are base catalyzed, such as the benzilic acid rearrangement.[19]

The reaction may also be viewed as a homolog of base-catalyzed ketone bromination,[20] in which the charge on oxygen participates during C–Br bond formation in a fashion analogous to an enolate. Reactions of homoenolates which are β-anionic ketones have recently been described.[21,22] Such species can be thought of as being derived from one extreme resonance form **23**, of an enolate such as **23** ↔ **31** by insertion of a tetrahedral carbon between the negatively charged atom and the π-electron system (Scheme VI). Apparently,

**Scheme VI**




when the stereochemistry of this system is arranged so that the reaction **25** → **26** involves little movement or added strain, such a valence tautomerization or resonance in fact does stabilize the anion produced by removal of a β proton. The alternative valence tautomerizations for such a species, **27–28** and **29–30**, have to our knowledge not been observed.[23]

(c) N. L. Allinger and J. L. Coke, *J. Org. Chem.*, **26**, 2096 (1961); (d) R. E. Pincock, E. Grigat, and P. D. Bartlett, *J. Amer. Chem. Soc.*, **81**, 6332 (1959), and references cited therein; (e) H. O. House and G. H. Rasmusson, *J. Org. Chem.*, **28**, 31 (1963); (f) N. L. Allinger, R. B. Hermann, and C. Djerassi, *ibid.*, **25**, 922 (1960); (g) N. L. Allinger and S. Greenberg, *ibid.*, **25**, 1399 (1960).

(16) (a) P. D. Bartlett and R. H. Rosenwald, *J. Amer. Chem. Soc.*, **56**, 1990 (1934); (b) M. Tiffeneau and B. Tchoubar, *C. R. Acad. Sci.*, **198**, 941 (1934); (c) M. Tiffeneau and B. Tchoubar, *ibid.*, 207, 918 (1938); (d) B. Tchoubar, *ibid.*, **208**, 355 (1939); (e) M. Tiffeneau, B. Tchoubar, and S. LeTellier, *ibid.*, **216**, 856 (1943); (f) M. Tiffeneau, B. Tchoubar, and S. LeTellier, *ibid.*, **217**, 588 (1943); (g) T. A. Geissman and R. I. Akawie, *J. Amer. Chem. Soc.*, **73**, 1993 (1951); (h) A. J. Sisti, *J. Org. Chem.*, **33**, 453 (1968).

(17) (a) S. Julia, M. Julia, H. Linarès, and J.-C. Blondel, *Bull. Soc. Chim. Fr.*, 1952 (1962); (b) C. R. Johnson, C. J. Cheer, and D. J. Goldsmith, *J. Org. Chem.*, **29**, 3320 (1964).

(18) C. J. Collins, *Quart. Rev., Chem. Soc.*, 14, 357 (1960).

(19) S. Selman and J. F. Eastham, *ibid.*, 14, 221 (1960).

(20) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, New York, N. Y., 1965, p 147 ff.

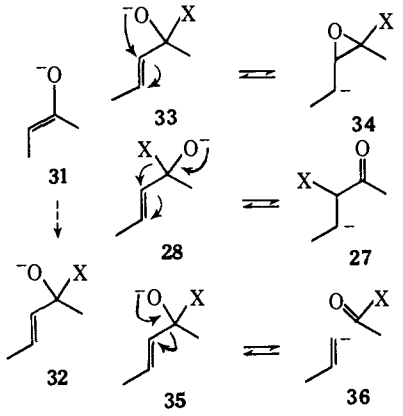
(21) A. Nickon, J. L. Lambert, R. O. Williams, and N. H. Werstiuk, *J. Amer. Chem. Soc.*, **88**, 3354 (1966), and references cited therein.

(22) (a) R. Howe and S. Winstein, *ibid.*, 87, 915 (1965); T. Fukunaga, *ibid.*, **87**, 916 (1965); J. P. Freeman and J. H. Plonka, *ibid.*, **88**, 3662 (1966); P. Yates, G. D. Abrams, and S. Goldstein, *ibid.*, **91**, 6868 (1969); (b) see also C. H. DePuy and F. W. Breitbeil, *ibid.*, **85**, 2176 (1963); and B. R. Davis and P. D. Woodgate, *Chem. Commun.*, 65 (1966).

(23) However, equilibrium has been observed for several α-hydroxy

It is also possible, however, to construct a second type of homoenolate, by homologization of the other extreme resonance form, **31**, of a typical enolate (Scheme VII). Such a homoenolate, **32**, is nothing more than

**Scheme VII**



an allylic alkoxide, but the reaction paths open to it may be represented by the same three types of valence-tautomeric reactions as were shown for **24**. While none of these has to our knowledge been observed as an equilibrium, at least two of them represent real pathways for irreversible reactions. This is indicated by the fact that the sequence **34** → **33** accurately describes the known and apparently irreversible base-catalyzed rearrangement of β,γ-epoxy esters[24,25] and nitriles,[25,26] as well as unactivated epoxides.[27] The sequence **35**–**36** is familiar in reverse as the addition of metallovinyl reagents to carbonyl compounds. The forward reaction seems much less favorable but might operate if either fragment of **36** had particular stability. The pyrolytic decarboxylation of certain aryl carboxylates may be construed as an example of this reaction.[28]

These three sequences apparently play no part in stabilizing allylic alkoxides themselves since allylic alcohols are not found to be appreciably more acidic than those of other types.[29] However, it will be observed that the three sequences shown for each homoenolate species involve, respectively, three-membered ring formation, substituent migration, and 2,3-bond cleavage, and thus correspond in their essentials to the three possible internal reactions of our bromonium alkoxide, leading to **8**, to **10** or **11**, and to **9**. Both of the products actually observed from this reaction are of the type derivable from **28**–**27**. We shall soon present data on reactions in a related system involving the formation of products corresponding to **34** and **36**.

## Experimental Section[30]

**Purification of Δ⁸-1-Phenyl-1-octalol (5).** Δ⁸-1-Phenyl-1-octalol (2.50 g), previously separated[3] by chromatography from other products of the reaction of **1** with phenylmagnesium bromide, was rechromatographed on 150 g of neutral $Al_2O_3$ (6% water added) and eluted with ether–hexane mixtures. Examination by nmr and by tlc ($SiO_2$, MeCN–PhH) of early, middle, and late chromatographic fractions gave no evidence of the presence of more than one isomer. Combination of the purest (tlc) fractions and distillation as described[3] gave 2.29 g of **5**, having spectral properties in agreement with those recorded.[3]

**Bromination of 4a.** Purified Δ⁸-1-phenyl-1-octalol (555.5 mg, 2.40 mmol) in 2.5 ml of dry ether in a 25-ml side-arm flask was cooled with an ice bath and stirred magnetically under $N_2$ during the addition of 2.60 ml (4.80 mmol) of 1.80 *M* phenylmagnesium bromide solution. The clear, pale brown solution was stirred at room temperature for 20 min and then recooled and a solution of 0.250 ml (4.80 mmol) of bromine in 3.0 ml of methylene chloride was added gradually with stirring. A red-brown color persisted increasingly toward the end of the addition so that no very clear end point was discernible. An aqueous solution of $Na_2SO_3$ and $NaHCO_3$ was added and the entire mixture was transferred to a separatory funnel and washed with this solution, with water, and with brine. Concentration of the dried organic extracts gave an oil whose infrared spectrum displayed bands both at 1720 and at 1680 $cm^{-1}$ (intensities approximately 2:1).

Extensive chromatography on neutral $Al_2O_3$ (2 or 3% water added) and elution with pentane and 3–5% ether–hexane or –pentane allowed the separation of 197.5 mg (27.7%) of bromo ketone **11**, mp 70–75° (eluted first). Recrystallization from pentane yielded material melting at 77–77.5°: ir 1680 $cm^{-1}$; uv 241 (ε 7400), 272 nm (640); nmr δ 1.1–3.0 (13 H complex), 4.85 (1 H, q, $J$ = 6 and 10 Hz), 7.45 (3 H complex), 7.75 (2 H complex).

*Anal.* Calcd for $C_{16}H_{19}BrO$: C, 62.55; H, 6.23. Found: C, 62.57; H, 6.36.

Further elution of the chromatograph provided 273 mg (36.5%) of bromo ketone **10**, mp 105–111°. A similar reaction, starting with 2.29 g of **5**, yielded 1.215 g (39.5%) of **10**. Recrystallization from pentane gave material melting at 110–111.5°, identical in all respects, including spectral data, with the material obtained from bromination of the crude Grignard product of **1**.[3]

**Catalytic Hydrogenolysis of 8-Bromo-9-phenyl-*cis*-1-decalone (10).** The second-eluted bromo ketone, **10**, from the above chromatograph (100 mg, 0.326 mmol) in 2.0 ml of MeOH was added to a slurry of 350 mg of 5% Pd/C catalyst, 200 mg of $NaHCO_3$, and 2.0 ml of MeOH which had been presaturated with $H_2$. The slurry was stirred at 25° under slight positive pressure of $H_2$ for 75 min, during which time 5.3 ml of $H_2$ was taken up. Filtration and concentration provided 61.5 mg (83%) of crystalline 9-phenyl-*cis*-1-decalone (**13**), mp 56–57°, whose melting point was raised to 56.5–57.5° by recrystallization from pentane. Both the melting point and ir of this material were identical (and mixture melting point was undepressed) with those of a sample similarly prepared from **10** obtained by brominating the crude Grignard product of **1**.[3] Spectral data for **13** are: ir 1705, 700 $cm^{-1}$; uv 259 (ε 240), 298 nm (105); nmr δ 1.3–2.9 (15 H complex), 7.2 (5 H, s).

*Anal.* Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83; mol wt, 228. Found: C, 84.33; H, 8.89; mol wt, 228 (mass spectrum).

**Attempted Equilibration of *trans*-9a-Carbomethoxy-7-methoxy-2,2-ethylenedioxy-1,2,3,4,4a,9a-hexahydrofluorene.**[31] The above compound (10 mg, 0.031 mmol) dissolved in 2.0 ml of MeOH was injected by syringe into a suspension of 35 mg of 5% Pd/C catalyst and 20 mg of $NaHCO_3$ in 2.0 ml of MeOH which had been presaturated with $H_2$. The mixture was stirred at room temperature under 1 atm of $H_2$ for 1 hr and then filtered, concentrated, and sublimed to give 8.8 mg of semicrystalline material. Analysis by vpc[32] (cis and trans were well separated) demonstrated that conversion to the cis isomer had occurred to the extent of less than 1%.

**Dehydrohalogenation of 8-Bromo-9-phenyl-*cis*-1-decalone (10).** Bromo ketone **10** (100.5 mg, 0.328 mmol) and dry lithium chloride

ketone cases (where the β atom in structure **27** is oxygen). See A. Nickon, T. Nishida, and Y. Lin, *J. Amer. Chem. Soc.*, **91**, 6860 (1969), and the references cited therein.

(24) W. W. Epstein and A. C. Sonntag, *J. Org. Chem.*, **32**, 3390 (1967).

(25) J. D. McClure, *ibid.*, **32**, 3888 (1967), and references cited therein.

(26) *Cf.* A. Padwa, D. Crumrine, R. Hartman, and R. Layton, *J. Amer. Chem. Soc.*, **89**, 4435 (1967).

(27) Y. Bessière-Chrétien and B. Meklati, *Tetrahedron Lett.*, 621 (1971), and references cited therein.

(28) F. H. Verhoek, *J. Amer. Chem. Soc.*, **61**, 186 (1939).

(29) (a) J. Hine and M. Hine, *ibid.*, 74, 5266 (1952); (b) P. Ballinger and F. A. Long, *ibid.*, **82**, 795 (1960).

(30) Melting points were determined with a Mel-Temp apparatus and are uncorrected. Infrared spectra were taken using a Beckman IR-10 or a Perkin-Elmer Model 21 or 421 spectrometer and, unless otherwise specified, in $CCl_4$ as solvent. Ultraviolet spectra were determined in 95% EtOH solution with a Cary Model 11 or 14 spectrophotometer; nmr spectra were taken with a Varian A-60 spectrometer ($CH_2Cl_2$ and/or TMS internal standard) and, unless otherwise specified, using $CCl_4$ or $CDCl_3$ as solvent. Mass spectra were determined with an AEI MS-9 or a Perkin-Elmer Model 270 mass spectrometer. Microanalyses were performed by Micro-Tech Labs, Skokie, Ill., and by Scandinavian Microanalytical Laboratories.

(31) H. W. Thompson, *J. Org. Chem.*, **36**, 2577 (1971).

(32) A 6 ft × 1/8 in. stainless steel column packed with 10% UC W98 silicone on 80–100 mesh firebrick was employed for this analysis.

(140 mg, 3.30 mmol) were heated in 1.0 ml of dimethylformamide under $N_2$ with stirring for 8 hr with an oil bath at 120°. Work-up by dilution with water and extraction with ether–pentane gave a yellowish oil on concentration of extracts. This oil, combined with the product of a similar dehydrohalogenation on 101.7 mg (0.332 mmol) of **10**, was chromatographed on 10 g of $Al_2O_3$ (3% water added). Elution with hexane–$CH_2Cl_2$ mixtures and combination of appropriate fractions gave material which was distilled in a short-path still at 125–135° (0.15 mm) to yield 107.2 mg (72%) of clear, pale yellow liquid, **12**. Greater than 90% purity was indicated by vpc: ir 1705, 710, 700 $cm^{-1}$; uv ($\epsilon$ at 210 nm = 9500), 259.5 ($\epsilon$ 289), 297 nm (120); nmr $\delta$ 1.2–2.8 (11 H complex), 5.5 (1 H, d of t, $J$ = 10 and 1 Hz), 4.2 (1 H, d of t, $J$ = 10 and 3), 7.2 (5 H, m).

**Hydrogenation of $\Delta^6$-9-Phenyl-*cis*-1-octalone (15).** $\Delta^6$-9-Phenyl-*cis*-1-octalone (**15**) was isolated in 28.5% yield by chromatography from the reaction previously described,[7] and melted 85–87° after recrystallization from hexane. This material (103 mg, 0.45 mmol) was stirred with 11 mg of 5% Pd/C catalyst in 3.0 ml of MeOH under $H_2$ at room temperature. After 35 min, uptake of $H_2$ had ceased (13.5 ml) and the solution was filtered and concentrated. Sublimation of the residue at *ca.* 100° (0.1 mm) gave a semisolid which was recrystallized from pentane to give 70 mg (67%) of **13**, mp 55.5–57°, undepressed on admixture with **13** prepared by hydrogenolysis of **10**. Further recrystallization provided material melting 60–60.5°.

**Catalytic Hydrogenolysis of 7-Bromo-8-benzoyl-*cis*-hexahydroindan (11).** A solution of 200 mg (0.652 mmol) of **11** in 4 ml of MeOH was injected into a suspension of 700 mg of 5% Pd/C catalyst and 400 mg of $NaHCO_3$ in 4 ml of MeOH which had been presaturated with $H_2$. The mixture was stirred for 1 hr at room temperature under 1 atm of $H_2$, then filtered and concentrated. The residue had strong ir absorption at 3620 $cm^{-1}$ but a weak band at 1675 $cm^{-1}$ as well as a sharp nmr singlet at $\delta$ 4.67 and a broad one at 4.09, indicating substantial carbonyl reduction. This material was reoxidized in 5 ml of acetone at ice-bath temperature with a solution prepared by diluting 2.67 g of $CrO_3$ plus 2.30 ml of $H_2SO_4$ up to a total volume of 10 ml with water.[33] The chromic acid solution was added dropwise with stirring until the orange color persisted for 1 min; then the mixture was diluted, neutralized, and extracted. Distillation of the concentrated ether extracts at 110° (0.15 mm) gave 115 mg (57.5%) of **16** as a colorless oil: ir 1675 $cm^{-1}$; nmr $\delta$ 0.9–2.9 (15 H complex), 7.35 (3 H complex), 7.75 (2 H complex); mol wt (mass spectrum), 228.

In subsequent experiments with 0.5 wt of catalyst, loss of bromine was found[32] to be essentially complete at 40 min without carbonyl reduction.

***cis*-Hexahydroindan-8-carboxylic acid (22).** 2-Carbethoxycyclopentanone (**17**)[34] was treated with methyl vinyl ketone for 24 hr in the procedure of Dauben and McFarland,[35] yielding 85.5% of distilled 2-($\gamma$-ketobutyl)-2-carbethoxycyclopentanone (**18**). This material was cyclized using aluminum *tert*-butoxide[13,36] and provided 29% of distilled 8-carbethoxy-5,6,7,8-tetrahydroindan-5-one (**19**), which appeared,[32] however, to be only about 60% pure. Hydrogenation of **19** in MeOH for 1 hr at atmospheric pressure over 0.1 wt of 5% Pd/C catalyst provided *cis*-8-carbethoxyhexahydroindan-5-one (**20**)[13] in 93% crude yield. Clemmensen reduction of **20** under the usual conditions[13,37] gave an 82% crude yield of *cis*-8-carbethoxyhexahydroindan (**21**). Saponification[13] of **21** afforded on neutralization of the basic aqueous extracts relatively pure[32] but liquid *cis*-hexahydroindan-8-carboxylic acid (**22**) in 70% crude yield. A portion of crude **22** was distilled, giving clear, colorless cis acid in 78% recovery.

***cis*-Hexahydroindan-8-carboxamide.** The above material, **22**, was identified as the *cis*-carboxylic acid by refluxing 400 mg (2.38 mmol) of it for 0.5 hr with 2.0 ml of $SOCl_2$ (16.8 mmol). Removal of excess $SOCl_2$ under vacuum was followed by condensation into the flask of several milliliters of anhydrous $NH_3$. The residue after evaporation of $NH_3$ was diluted with ether, washed with water, and concentrated to give 234 mg (58.5%) of the amide, mp 106–107°. Recrystallization from hexane gave white needles, mp 108–109° [lit. mp 114–115°,[38] 111–112°[13] (trans amide, mp 123.5–125, 123–124°[38])].

**8-Benzoyl-*cis*-hexahydroindan (16).** A solution of 648 mg (3.86 mmol) of **22** in 5 ml of dry dimethoxyethane was added to a stirred suspension of 40 mg (5.0 mmol) of LiH in 5 ml of dimethoxyethane and the mixture was refluxed under $N_2$ for 2.5 hr (white precipitate). The mixture was cooled with an ice bath and 3.0 ml (4.13 mmol) of 1.38 *M* ethereal phenyllithium was slowly added to the stirred suspension.[14] After the mixture had been stirred for 2 hr at room temperature it was poured into a vigorously stirred solution of 0.5 ml of concentrated HCl in 10 ml of water. The mixture was saturated with NaCl and extracted with ether, and the ether layer was washed with 10% NaOH, dried, concentrated, and distilled at 110° (0.02 mm) in a short-path still to give 442 mg (50.3%) of colorless oil: ir and nmr identical with those of the hydrogenolysis product of **11**; uv 241 ($\epsilon$ 6200), 272 nm (700).

*Anal.* Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83; mol wt, 228. Found: C, 84.07; H, 8.91; mol wt, 228 (mass spectrum).

In addition to identical ir and nmr spectra, the two samples of **16** (synthetic and hydrogenolysis product) had identical vpc retention times[32] and their mass spectra showed only negligible differences. Parent ion (*m/e* 228) intensity expressed as a percentage of total intensity for all ions with $m/e \geq 50$ was 2.00% for synthetic **16** and 2.02% for hydrogenolysis product **16**.[39]

When synthetic **16** and hydrogenolysis product **16** were refluxed with 1 equiv of $NH_2OH \cdot HCl$ in EtOH–pyridine the same solid was produced, mp 125–143° after recrystallization from aqueous EtOH, unchanged by sublimation, further recrystallization, or treatment with anhydrous HCl in ether. Analysis by vpc[32] showed in each case the same two peaks of about equal area, believed to represent the syn and anti oximes.

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